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PREPARATION AND
CHARACTERIZATION OF
LOW DP END-CAPPED
PYRRONE MOLDINGS

by C. T. Hughes

Prepared by
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16. Abstract

Pyrrone polymers were studied to determine their utility as structural molding resins. Because of the problems previously associated with the molding of these resins, a major portion of the work was in a novel synthesis route. This route based on the idea of making short chain fully cyclized precursor molecules which are then chain extended and the newly formed bonds cyclized during the mold cycle. The molding process was studied in considerable detail with over 175 moldings made for physical, mechanical and/or thermal characterization as well as delivery to NASA-Langley. The mechanical properties of the best moldings were exceptional in high temperature properties. Filled moldings were made with particulate fillers including colloidal silica, carbon, graphite, MoS_2 powder, and industrial diamonds. Flexural tests were obtained on some of these composites.

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FOREWORD

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Research Section, served as Project Manager.

TABLE OF CONTENTS

LIST OF TABLES

I. INTRODUCTION

Many novel polymer structures have been studied in recent years to find thermally and structurally superior resins.[1-5] The majority of commercial uses have thus far been filled by the polyimides which have good thermal and structural properties and relative ease of fabrication. The polybenzimidazoles have also been studied extensively but poor resistance to oxidation has limited their use. However in the search for the ultimate in thermal stability, theoretical considerations suggest that the more complex, double-stranded polymers[6] of which the polyimidazopyrrolones is a typical example, should be superior to the polymides and polybenzimidazoles, both of which contain higher proportions of single bonds. (See Figure 1). These polymers, which are commonly called Pyrrones, may be full ladder or step ladder in overall structure, depending on whether there are single bonds in either of the monomers.

The predicted superiority of such double-stranded polymers has been indicated only for very thin films and fibers.[7,8] The inability to achieve the desired properties in the potentially useful moldings or laminates[7], in addition to excessive release of volatiles during cure, has seriously hampered a full evaluation of these polymers. All of the early preparation of Pyrrones[3,7,9-12] utilized the solution route used successfully for preparing the polyimides. This route involves the formation of high-molecular weight precursor polymers in which the polymer formation is interrupted at the uncyclized amide-acid stage (Figure 2). The flexibility in the polymer backbone derived from the three single bonds of the amide polymer imparts solubility and flow to the molecule; this, in turn, permits relatively easy fabrication techniques. This tractibility can also be obtained to a somewhat equivalent extent in the Pyrrones by stopping the reaction at the amide-acid-amine form (Figure 2).

There are two problems associated with the Pyrrones. The release of two moles of water in curing to the Pyrrone group doubles the amount of volatiles released in comparison to the polyimide cure, thus compounding the problems in fabricating large specimens. A more subtle, yet equally troublesome trait of working with the Pyrrones is the likelihood of cross-linking or some similar interaction between the amino and the acid groups which exist in the precursor polyamide. Such interaction could lead to reduced processability and/or lowered thermal stability.

This report describes the results of an investigation of a fundamentally different approach to the formation of high molecular weight, fully cyclized, Pyrrone polymer. The conventional route described above is characterized by an initial polymerization step, followed by the cyclization step during the cure. These steps can be represented as shown in Figure 3. The approach taken in this investigation involves an initial step which leads to low molecular weight, fully cyclized oligomers which are later polymerized and the cyclization completed during the cure step (Figure 3). Thus at lease a portion of the cyclization and attendant release of volatiles is accomplished prior to the synthesis of a high molecular weight polymer species.

POLYIMIDE

POLYBENZIMIDAZOLE

PYRRONE

Figure 1

POLYAMIC ACID

POLYAMIC-ACID-AMINE

Figure 2

MONOMERS ⟶ CYCLIZE ⟶ LOW DP CYCLIZED OLIGOMERS

POLYMERIZE

POLYMERIZE AND COMPLETE CYCLIZATION

PRECURSOR POLYMER A-A-A FORM ⟶ CYCLIZE ⟶ PYRRONE POLYMER

Figure 3

ANHYDRIDE CAPPED OLIGOMER

AMINE CAPPED OLIGOMER

70-0226

Figure 4

2
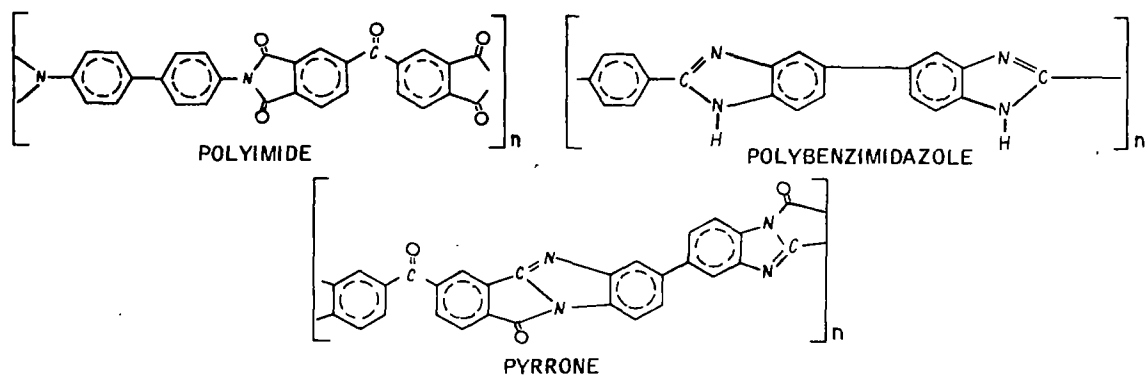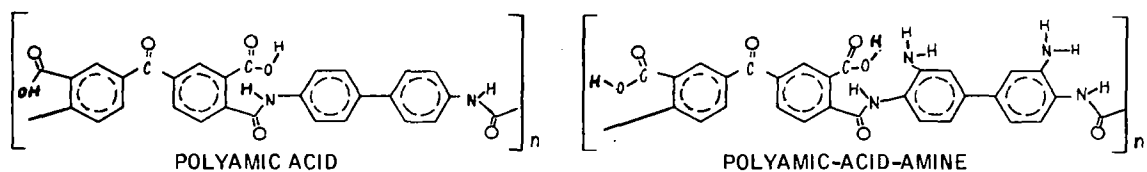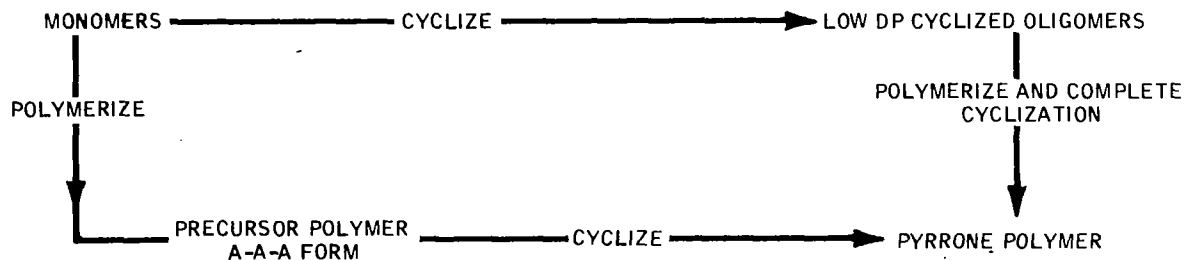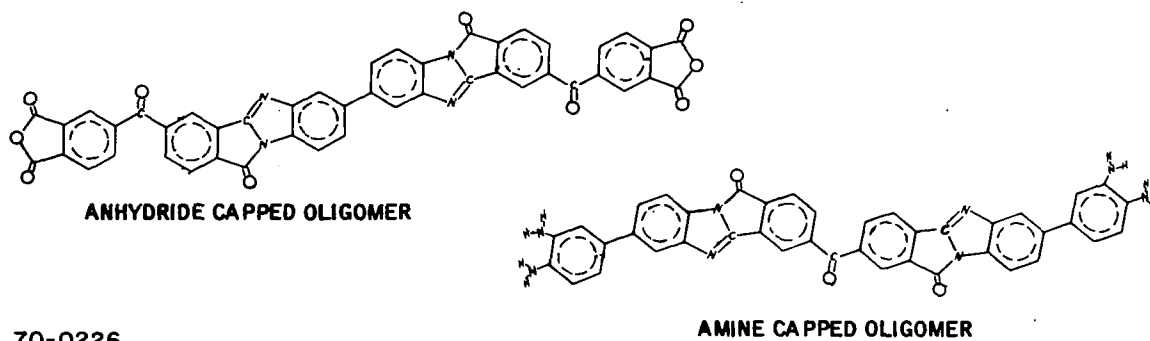
The process is actually more complex than indicated in Figure 3 since the low DP (degree of polymerization) oligomers must be made as separate amine end capped and anhydride end capped materials for stability, as well as for control of chain length. These oligomers must then be mixed on a molecular scale in such a fashion that chain extension (polymerization) is minimized prior to the curing cycle. The desired DP for the oligomers depends upon the internal flexibility of the monomers and the end product. Enough flow character must be present to permit the participation of the mixed oligomers in the chain extension reaction, wetting of reinforcement or filler surfaces, and to fill voids left by release of volatiles and shrinkage effects. The higher the DP of these oligomers the less is the volatile problem. For example, oligomers of DP 1-1/2 have only a third the volatiles of the conventional route resins; higher DP oligomers have lower volatile content. However, the flow characteristics of fully cyclized material drops drastically with increasing DP because of the high rigidity in the polymer backbone. Thus the initial work was done using monomer ratios which would give an average DP of 1-1/2. If the oligomers are synthesized under conditions that promote complete cyclization, the likelihood of branching reactions is decreased to some extent as the volatile content. Figure 4 shows the structural formulas of both anhydride and amine end-capped oligomers of DP 1-1/2, which were the initial synthesis goals of this program.

II. INITIAL SYNTHESIS

The pyrrones can be formed from the reaction of a wide variety of tetraacids and tetraamines. The monomers which were used in this investigation were 3,3'-4,4' benzophenone tetracarboxylic acid dianhydride (BTDA) and 3,3'-4,4' tetraminobiphenyl (DAB). The work which was reported in reference 10 was used as a basis for picking the reaction temperatures for the formation of partially or fully cylized oligomers. It was pointed out that the imide ring formation (the second step in the desired reaction sequence) starts to take place with a significant rate above 150°C and the final pyrrone ring formation requires temperatures above 200°C. However, the initial oligomer synthesis attempts were made at room temperature in dimethyl formamide (DMF) to get first hand information about the onset and the extent of gellation. A 2:1 monomer ratio (anhydride to amine) was used for the initial synthesis of anhydride capped oligomer which was considered the more critical of the two because of the high reactivity of the end groups. This should give an average degree of polymerization (DP) i.e., number of repeat units in the chain, of 1-1/2. The anhydride end capped oligomer solution gelled before the complete addition of the amine. The data for these and similar initial experiments are given in Table I. This established that the branching reaction does indeed occur and rapidly at room temperature if the local stoichiometry is changed from 1:1 and corroborates the literature data in which gellation occurs when anhydride is in excess. Consistent with this thesis is the much lower gel formation observed in experiment 3 which was run at room temperature but at one tenth the concentration of the previous runs. The amine capped oligomer (Experiment 478-49) in contrast gave only some slight amount of gel particles immediately though complete gellation did occur after three weeks at room temperature. This probabily means that the amine groups react much more rapidly with the anhydride end groups than with acid groups. Attempts were made to extract nongelled low DP oligomers from the above solutions and gels with only partial success.

Oligomer synthesis in refluxing DMF (b.pt. 155°C), shown in Table II, gave further evidence for the idea that the synthesis should be done under conditions that promoted complete or nearly complete cylization within the chain. The oligomer should go through the amide-acid-amine stage to the imide-amine form in the refluxing DMF. This should reduce the extent of gellation in the ahhydride capped oligomer and possibly eliminate it in the amine capped oligomer. The anhydride end-capped oligomer showed only small amounts of gel particles but was very viscous while the reaction mass from amine capped oligomer was very low in viscosity and had even less gel. Initial attempts at purification did not give a well defined crystalline product. Perhaps this is due to the formation of a mixture of isomers, three of which are possible. However, the paper chromatograms showed narrow bands for the amine capped oligomer. The much lower quantitites of gel and the very low viscosity of the amine capped oligomer solution appears to substantiate the contention that gel formation is due to reaction of the free amine with anhydride end groups in the amide-acid-amine precursor and that the imide-amine intermediate reduces this branching reaction. Anhydride capped oligomer in the imide-amine form gave a negative test for

4

TABLE I

PREPARATION OF AMIDE-ACID-AMINE FORM (A-A-A) PYRRONE OLIGOMERS

Experiment No.	End Cap	Monomer Concentration	Remarks
478-48	Anhydride	0.4M	Complete gellation after 70% of amine addition
478-45	Anhydride	0.4M	Complete gellation after 80% of amine addition
478-47	Anhydride	0.04M	Very small amount of gel; impractical concentration
478-49	Amine	0.4M	Very small amount of gel immediately; complete gellation after 3 weeks at room temperature

NOTE: All oligomers were prepared at room temperature in Dimethyl Formamide (DMF)

TABLE II

PREPARATION OF IMIDE-AMINE (I-A) PYRRONE OLIGOMERS

Experiment No.	End Cap	Reaction Temperature °F	°K	Remarks
478-52	Anhydride	295	(419)	Little gellation but very viscous
478-70	Anhydride	300	(422)	Slight gellation
478-88	Anhydride	300	(422)	Complete gellation; 5 hour addition time; concentration reached 0.6M just prior to gellation; DMF distilled off as DAB solution added.
478-89	Anhydride	300	(422)	Complete gellation; 15 min. addition time; concentration reached 0.5M at time of gellation; DMF distilled off as fast as DAB solution
478-54	Amine	295	(419)	Slight gellation; low viscosity
478-71	Amine	300	(422)	No gellation

Note: All oligomers were prepared in refluxing DMF at 0.4M concentration except as noted in remarks.

for aromatic-amine. This lack of normal amine activity may be due in part to steric hindrance but is more likely due to hydrogen bond ring formulation. Attempts to use N-methyl pyrrolidone (NMP) and dimethyl sulfoxide (DMSO) as high boiling solvents to get direct reaction to the imidazopyrrolone structure went awry due to degradation of the solvent or reaction of the solvent with the monomers under reflux conditions.

Infrared spectra of the product from the reactions run at room temperature in DMF were obtained on films made by vacuum drying the DMF solution on a salt plate. These spectra were made at room temperature and again after heating for 30 minutes at 200°F, 300°F, 400°F, 500°F, and 600°F. These spectra, Figure 5, show the gradual changes from A-A-A to pyrrone structure. The major changes are the very large reduction in carbonyl absorption at $1250 \cdot cm^{-1}$ and the increase in imide band at $730 \ cm^{-1}$. The imide and imidazole bands at $1760 \ cm^{-1}$ and $1620 \ cm^{-1}$ respectively are not so apparent. It is possible that they are masked by the strong anhydride bands at $1690 \ cm^{-1}$ and $1780 \ cm^{-1}$ which are increasing along with the $1865 \ cm^{-1}$ anhydride band as the heating time and temperature increase. The spectra of oligomer from experiment 478-52 (BTDA capped; refluxing DMF) was similar to that of the 300°F spectra described above. This is as expected since the temperature of the refluxing DMF solution was 145°C (293°F). While it appeared that cyclization had taken place beyond the A-A-A form and that this improved the synthesis reaction, some branching and/or crosslinking was still taking place. The synthesis temperature was still below that believed necessary for complete cyclization to the pyrrone form (except for the experiment with NMP in which solvent degradation occurred). Thus a search for other solvents with higher boiling points and/or better stability was conducted.

Polyphosphoric acid (PPA) was considered because of its value in promoting the acid-amine reaction in preparing the BBB polymers,[8] but the extremely low solubility of the monomers in the PPA militated against trying it and the concentrated sulfuric acid was tried instead. An anhydride capped oligomer synthesis was successful to the extent that no gel was observed and the test for aromatic amine was negative. This latter test was especially fruitful because it indicated that a substantial cyclization had indeed taken place. However, complete removal of the sulfuric acid could not be obtained despit repeated washing or extraction with water. Perhaps the sulfuric acid was reacting with the amine or the aromatic nuclei to form sulfamides or sulfonic acids. Nonetheless the system was abandoned when it was found that the acid caused complete gellation during synthesis of the amine capped oligomer. Figure 6 shows the infrared spectrum of anhydride capped oligomer made in concentrated sulfuric acid with BTDA in the reference beam.

The lack of immediate success with the inorganic acid solvents started a further look at the polar organic solvents. DMF was considered for use at above ambient pressure (500-700 psig) so that the boiling point would be raised to $\sim$ 200°C. Hexamethyl phosphoramide (HMP) with a boiling point of 220°C was also tried as a solvent. The high pressure DMF runs were made in stainless steel pressure vessels with a nitrogen atmosphere to

VACUUM DRIED

200°F

300°F

400°F

500°F

600°F

2000   1500   1000   700
FREQUENCY (CM^{-1})
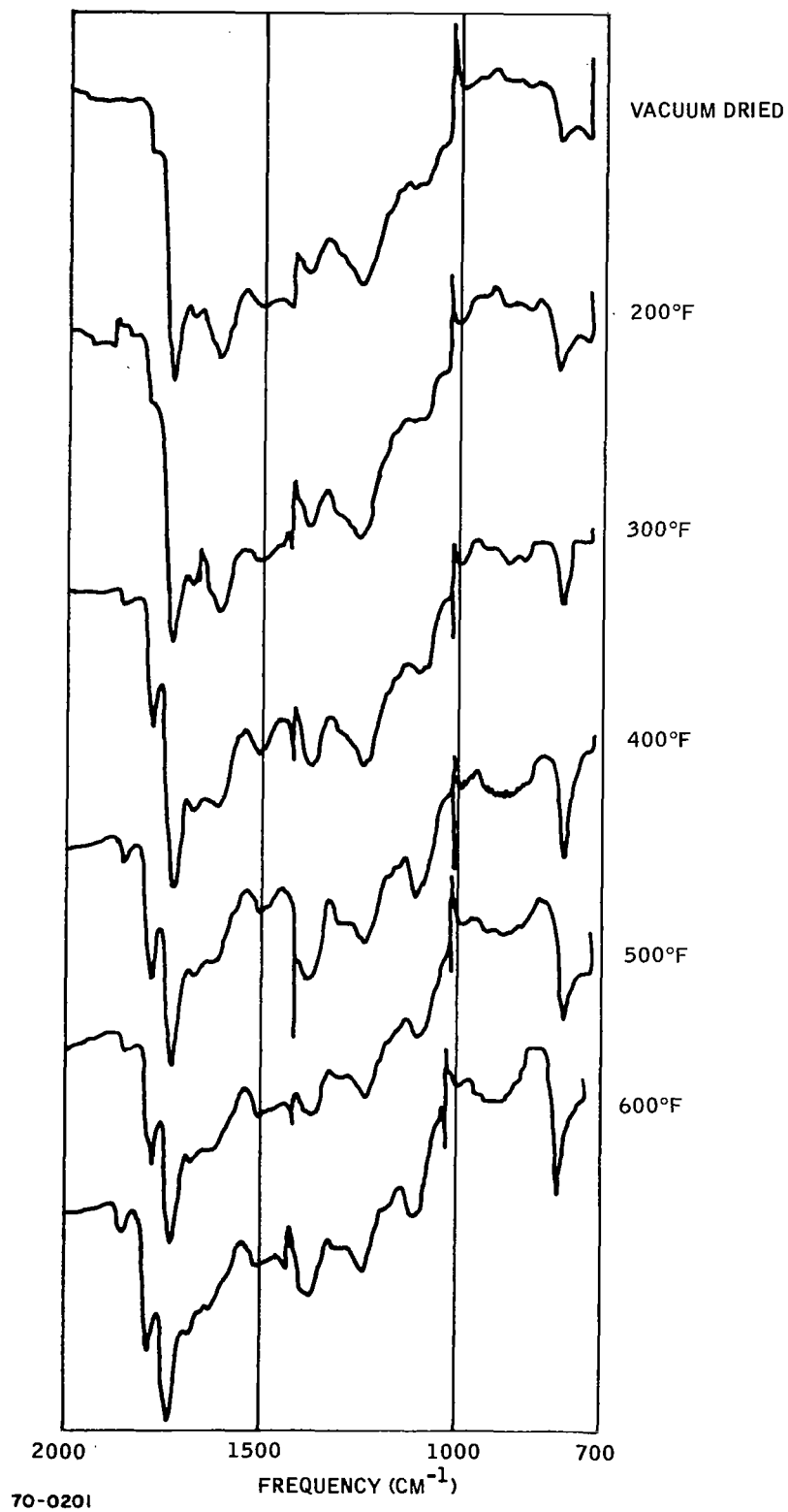
70-0201

Figure 5 IR SPECTRA OF ANHYDRIDE CAPPED OLIGOMER WITH 2:1 MOLE RATIO
HEATED TO VARIOUS TEMPERATURES

8

2000   1700   1400   1100   800
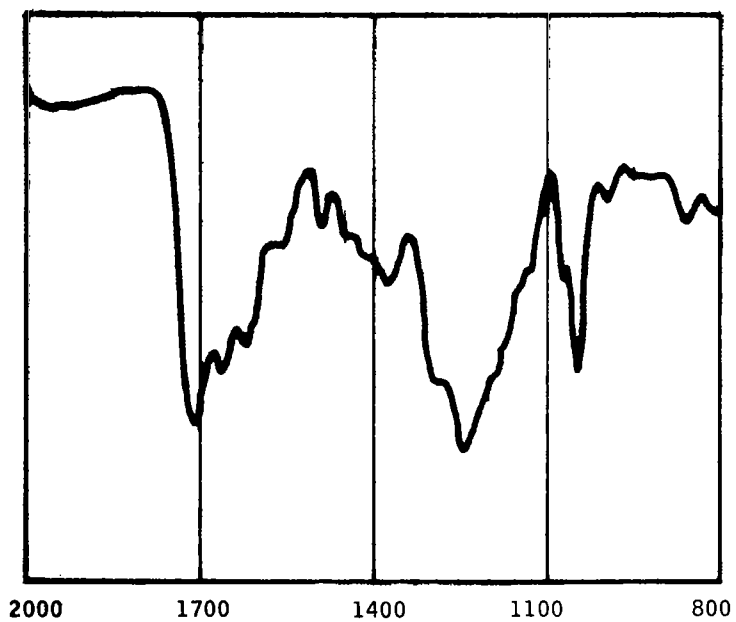
FREQUENCY (CM^{-1})

70-0203

Figure 6 IR SPECTRA OF ANHYDRIDE CAPPED OLIGOMER
SYNTHESIZED IN SULFURIC ACID

2000   1700   1400   1100   800
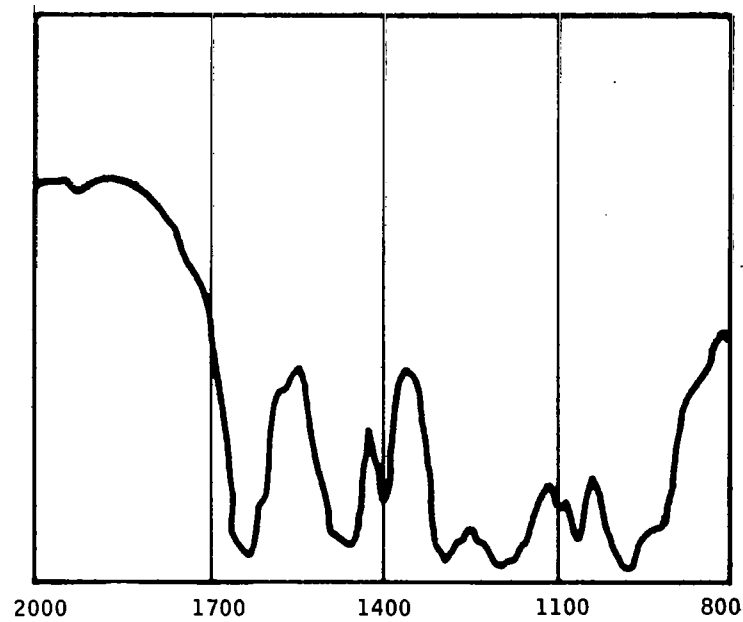
FREQUENCY (CM^{-1})

Figure 7 IR SPECTRA OF ANHYDRIDE CAPPED OLIGOMER
SYNTHESIZED IN HMP

6

raise the pressure to the 500-700 psig range. Initial trials were made by mixing the two solutions in a nozzle and then flashing the mixture to atmospheric pressure. However, the high pressure DMF solvent runs, both anhydride and amine capped, and the hexamethyl phosphoramide high temperature run gave negative results. The product in each case was water soluble and gave positive tests for aromatic amine. IR spectra were substantially different than those from insoluble resin as shown in Figure 7. It appeared that the water from the initial imide ring formation was kept available for hydrolysis and the resulting equilibrium was not in favor of full cyclization.

A second method tried, using cyclohexanone as a poor solvent in which the two monomers (BTDA and DAB) were just soluble at the boiling point, hoped that any reaction products would precipitate immediately. The low mobility in the solid state should reduce branching substantially and might well eliminate it entirely. The product of this experiment was an orange precipitate which formed immediately upon addition of the boiling amine solution to the boiling anhydride solution. The IR spectrum of this product showed the correct peaks for anhydride end groups and strong indication of imide rings but also showed some solvent remaining even after prolonged heating under vacuum. A repeat experiment with cyclohexanone led to the overall resin recovery of only 50 percent; therefore this solvent was abandoned to look for higher boiling solvents.

It appeared possible that another acidic solvent but one which was not reactive to the benzene ring might have the advantages but not the disadvantages of sulfuric acid. Sulfonic acids fit this criterion but the one suggested in reference 8 (methane sulfonic acid) had too low a boiling point (only 167°C) to permit reaction all the way to the pyrrone structure. Consideration of the sulfonic acids was started with benzene sulfonic acid (BSA) since it was at least relatively stable to 200°C and had a much lower melting point (50°C) than did the P-toluene sulfonic acid (106°C).

The next run, Experiment 478-95 (Table III), was made therefore in BSA which is a strong acid but is not a sulfonating agent. Experiment 478-95 was run at half the concentration of the previous runs with a double condenser and a 25 percent excess of BTDA (mole ratio 2.5:1). This latter change was made to reduce the average DP of the product. No gel was seen. However, the isolation procedure was more complicated than anticipated. The reaction solution was initially poured into a large volume of cold water. A light colored flocculent precipitate separated immediately but changed to a dark colored syrup as the ratio of reaction solution to water approached 1:3. The dark syrup could be changed to the light colored precipitate by mixing with more water in a blender. However, the removal of the BSA hit a snag when the pH of the wash water rose to about 3.5. Here a large portion of the precipitate became dispersed apparently in colloidal suspension, because precipitation would not occur even under centrifugation. Due to the large amount of washing coupled with the separation problem, extraction was tried to remove the BSA. Both water and acetone are successful but each has its advantages and disadvantages. The acetone extracts most of the BSA more quickly but the water does a more complete job. The acetone was tried in the
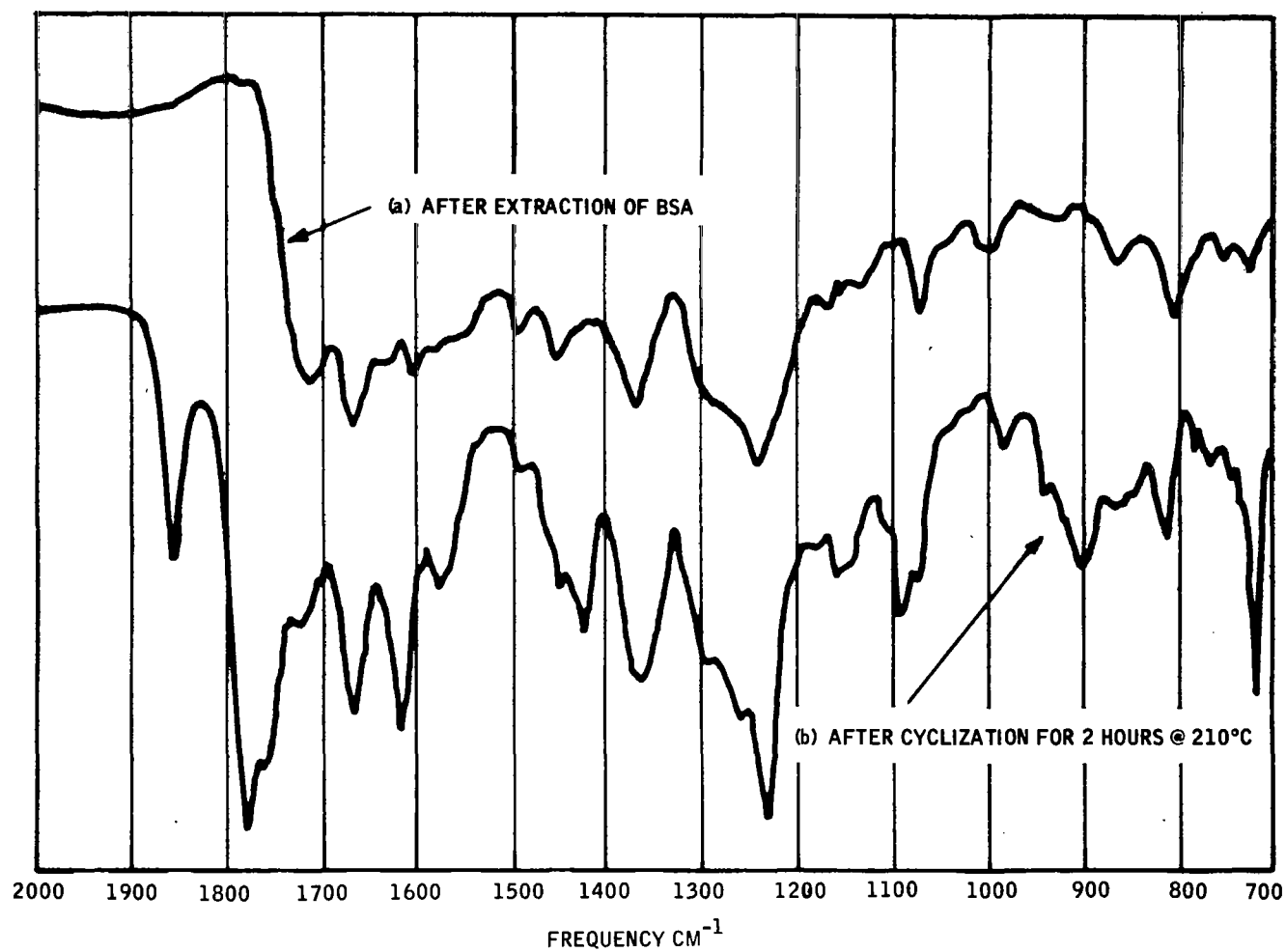
Figure 8 IR SPECTRA OF ANHYDRIDE CAPPED OLIGOMER WITH 2.5:1 MOLE RATIO SYNTHESIZED IN BSA

70-0204

11

TABLE III

EFFECT OF BSA SOLVENTS ON OLIGOMER SYNTHESIS

Exp. #	End Capped	Mole Ratio	Conc.	Temperature	Solvent	Benzene given off	Remarks
478-95	Anhydride	2.5/1	.2M/ .25M	210°C	benzene sulfonic acid; highest purity(HP)	yes	Resin light green (ppt. into H$_2$0)
478-99	Anhydride	2.5/2	.2M	210°C	BSA; refined technical	yes	Resin black (ppt. in acetone)
478-102	Amine	2.15/1	.2M	170°C	BSA (HP)	no	Dark orange (ppt. into acetone)
478-103	Amine	2.15/1	.24/ .3M	170°C	BSA (HP	no	Resin dark orange (ppt. into acetone)
478-106	Anhydride	2.01/1	0.2M	200°	BSA (HP)	yes very slight amount	resin light yellow green in H$_2$0; light orange in Acetone (ppt. in H$_2$0 80% and acetone 20%
478-110	Amine	2:1	0.2M 0.3M	200°C	BSA; refined technical		Decomposition occurred in monomer solutions before oligomer synthesis

12

hopes that hydrolysis of the end groups would not occur, thus eliminating the extra step of cyclization under vacuum. Unfortunately, the IR spectra of the acetone washed product shows strong acid bands (see Fig. 8 (a)) though the hydrolysis may have taken place during the initial precipitation in water. Figure 8 (b) shows the reappearance of the anhydride bands and the intensification of the imide and imidazole bands after heating in vacuum at $210^{\circ}C$ for 2 hours. It is interesting to note that the acetone washed material is a light greenish white color that turns to bright orange yellow when heated to $210^{\circ}C$ under vacuum. The orange yellow color turns to greenish again when extracted with cyclohexanone but returns when reheated to $210^{\circ}C$.

By using BSA as solvent it is possible to synthesize the oligomers at such temperatures that the reaction appears to go directly to the pyrrone form without side chemical effects or the necessity of high pressures. Samples from Exp. 478-95 and Exp. 478-104 showed no sulfur after extraction with water and drying. Furthermore there was no evidence of gel in any runs made in BSA. These synthesis data and solvent removal data are listed in Tables III and IV respectively. The IR spectra of the dried "anhydride" capped oligomer from Exp. 478-95 showed substantial carboxylic acid bands from hydrolysis of the end groups. Heating to recyclize the anhydride groups, extraction of this with cyclohexanone to remove excess BTDA and reheating to $210^{\circ}C$ gave the spectra shows in Figure 9 (a). This is very similar in features to that shown in Figure 8(b) which was not extracted but with major BTDA bands gone. Features of major interest are the anhydride peaks at 1860 cm^{-1}, 1780 cm^{-1}, the imide peak at 715 cm^{-1} and 1760 cm^{-1} and the imidazole peak at 1620 cm^{-1}. The amine capped oligomer shows a very well defined imide band at 1750 cm^{-1} but the imide band at 720 cm^{-1} and the imidazole band at 1620 cm^{-1} both appear broadened by ill defined small bands as shoulders. These features are shown in Figure 9 (b).

The problem of precipitation of BSA material with intermediate pH was solved in two ways. The first solution went through the critical pH range in a soxhlet extractor using either water or acetone. The second solution was to wash with 0.4N HCl (pH of ~1) followed by a washing with distilled water. The settling remained rapid throughout seven wash cycles which, with the centrifugation to speed the settling, was done in 4 hours. Overnight extraction with water gave a sulfur free product. This latter method is probably more feasible for large scale operation than the extraction technique.

In parallel with the polymerization studies, work to improve monomer purity and to define the effect of monomer purity on the oligomers and final moldings was pursued. The study of the effect of monomer purity showed no significant difference in operation of the synthesis. Resin color and precipitation behavior for the recrystallized monomer did not appear different from the DMF made material or the "as received" monomers run in BSA.

TABLE IV

EFFECT OF OLIGOMER WASHING PROCEDURE ON SULFUR CONTENT

Exp. #	Solvent	Liquid used in Precipitation	Liquid used for Extraction	Time of Extraction	% Sulfur
478-95	no additional purification	H_2O	Case I Acetone Case II H_2O	10 days 7 washings	0.0% 0.0%
	low in heavy metals from DPI; monohydrate				
478-102	no additional purification	H_2O	H_2O	7 days	0.0%
	low in heavy metals from DPI; monohydrate				
478-104	no additional purification	H_2O	H_2O	7 days	0.0%
	low in heavy metals from DPI: monohydrate				
478-106	no additional purification	H_2O	Case I 20 hrs. H_2O Case II 20 hrs. Acetone		2.0% 1.8%
478-99	no additional purification	H_2O	Acetone	8 days	3.45%
	Refined Technical (poor quality)				
478-110	as received Refined Technical (poor quality)	*			

*Product was like black mud and extraction gave no useful resin
Resin was made in stainless pressure vessels with mixing in high shear gun; gross solvent degradation occurred.

14

9(a)

9(b)

2000 1900 1800 1700 1600 1500 1400 1300 1200 1100 1000 900 800 700

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70-0205
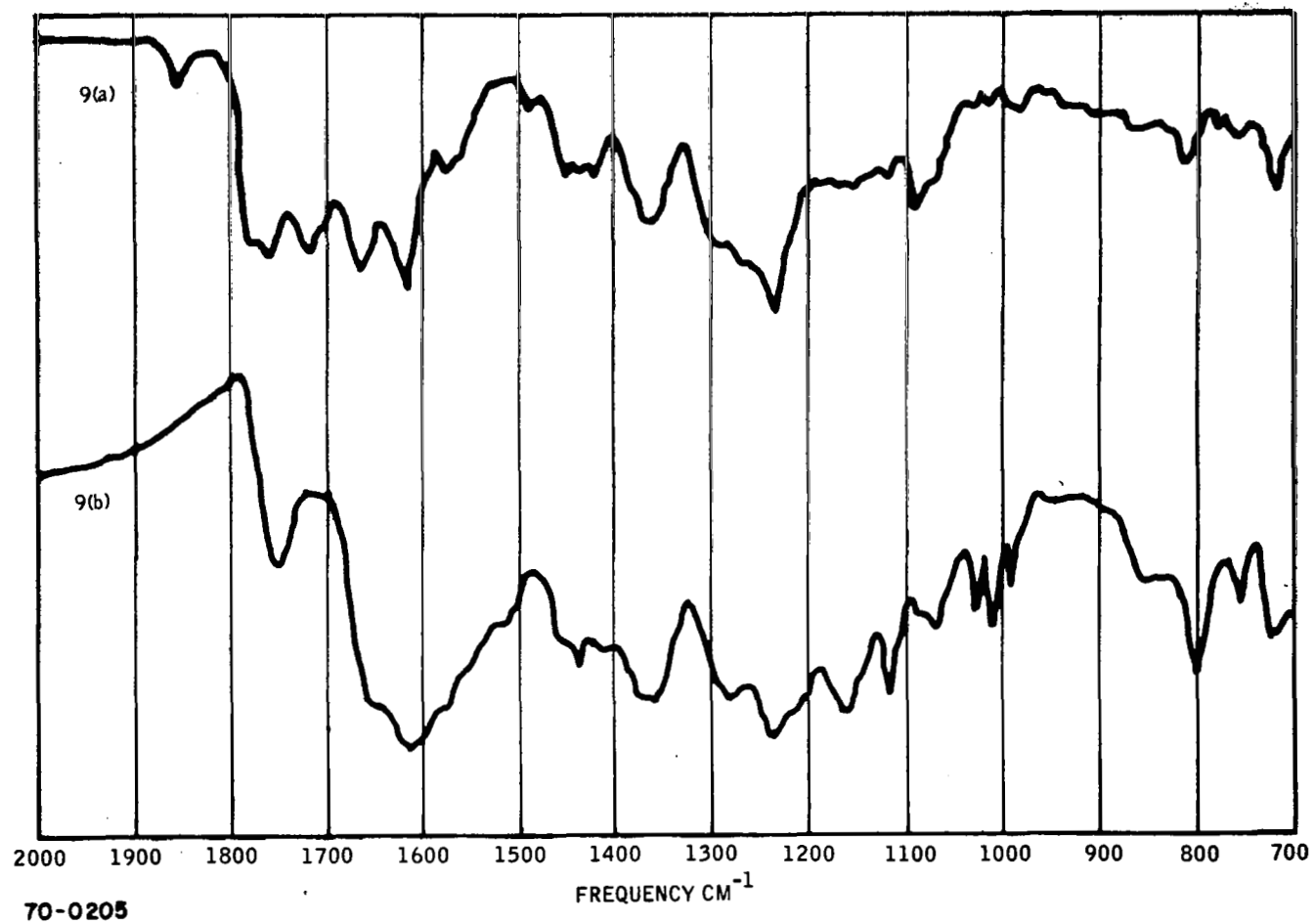
Figure 9 IR SPECTRA OF ANHYDRIDE CAPPED OLIGOMER (UPPER) AND AMINE CAPPED OLIGOMER (LOWER) EACH SYNTHESIZED IN BSA

TGA curves were obtained on many of the early oligomers as part of a continuing effort to characterize the material. Significant differences in the curves of the early oligomers are shown in Figure 10. Both the curves appear to have three dips in them but the temperature at which the changes occur and the magnitude of the changes vary considerably. Experiment 478-59 (Fig. 10 (a) made in concentrated sulfuric acid, shows three quite prominent dips with the largest at 120°C, the second at 500°C and vestiges of one at 700°C. Although Experiment 478-63 (Fig. 10 b) was also carried out in DMF at 205°C the first dip is at ∿ 75°C, the second at 300°C, a third at about 500°C and possibly the hint of a fourth at 700°C. Attempts at identifying the material lost at these dips in the curves by gas chromatography and pyrolysis in a special IR cell failed. Whether this was due to the fragments being too high in molecular weight and therefore not sufficiently volatile or other problems was never defined. Instrument sensitivity is probably not the main reason since material in smaller quantities than the dips indicated have been examined by these techniques many times in our laboratories.

The molecularly mixed oligomers generally have shown a more complex TGA curve with four breaks in the curve. Typical is the curve from Figure 11 run in helium of 478-114A (Experiment 37-38) which has dips at about 50°C, 200°C, 500°C, and 700°C. The companion curve of the same material done in air (Fig. 11) makes a very interesting comparison. The similarity of the curves out to 500°C both level and shape indicates that the oxidation up to that temperature is either inconsequential or at least very slow relative to the test time at temperature above 350°C. This speculation of relatively slow oxidation rate is corroborated by the relatively little charring seen in flexural test samples done at 700-1000°F (370-540°C). The flexural test samples see the final test temperature for 15-30 minutes and yet retain the brownish color they had at the start. Even test sample fragments that remained in the oven over several test periods, perhaps 2-3 hours at 1000°F, have not been completely charred.

Figure 12 shows the effect of the pH level of the washed powder and the molecular mixing temperature on the thermal stability as measured by TGA data. 478-126A was made by mixing at 110°C and washing to ph 1.5-2.0, 478-126C was also mixed at 110°C but was washed to ph 4.5 and 478-130A was mixed at 170°C and washed to the low ph value (1.5-2.0). All of the resin came from the same runs (Experiment 478-126). The extra acid left behind, in washing only to the low ph (1.5-2.0), appears to cause an extra weight loss starting about 300°C. Both the air and helium runs on the low pH material show an extra dip over the high pH material in this range. The result is that the low pH material has 8-10 percent more weight loss at 500°C than the high pH material. There appears to be no significant difference whether the molecular mixing temperature is 110°C or 170°C. At most there is a slight shift to lower temperature in this dip as the molecular mixing temperature goes up.

16

TGA DATA (10a)

SAMPLE FORM	POWDER
HEATING RATE	10°C/M
ATMOSPHERE	HELIUM

SAMPLE NO. 478-59

BTDA CAPPED FROM H_2SO_4 @ 212°C

10a

TGA DATA (10b)

SAMPLE FORM	POWDER
HEATING RATE	10°C/M
ATMOSPHERE	HELIUM

SAMPLE NO. 478-63

BTDA CAPPED FROM DMF @205°C

10b
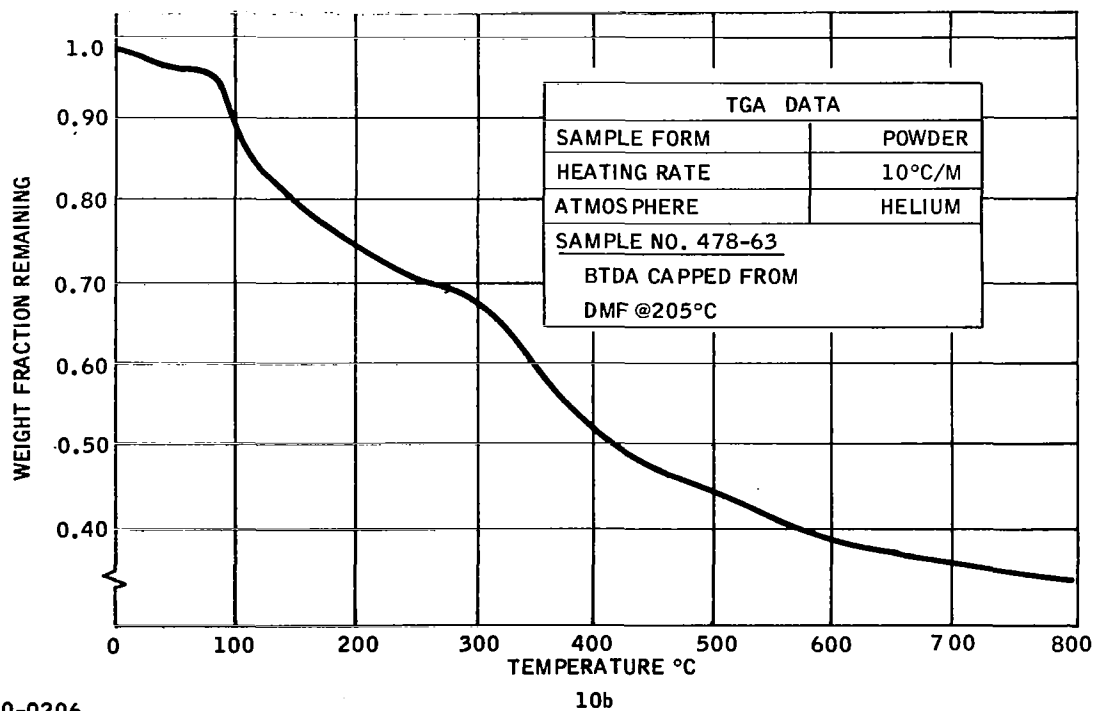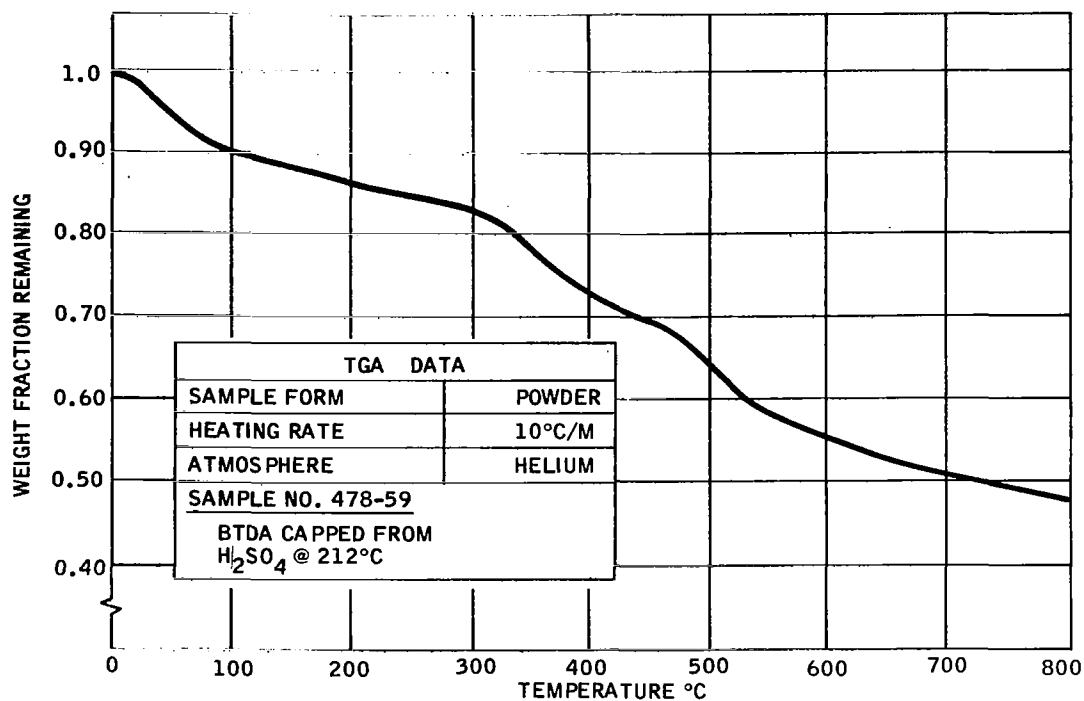
70-0206

Figure 10 TGA ANALYSIS OF ANHYDRIDE CAPPED OLIGOMERS FROM H_2SO_4 AND HIGH PRESSURE DMF SYNTHESES

17
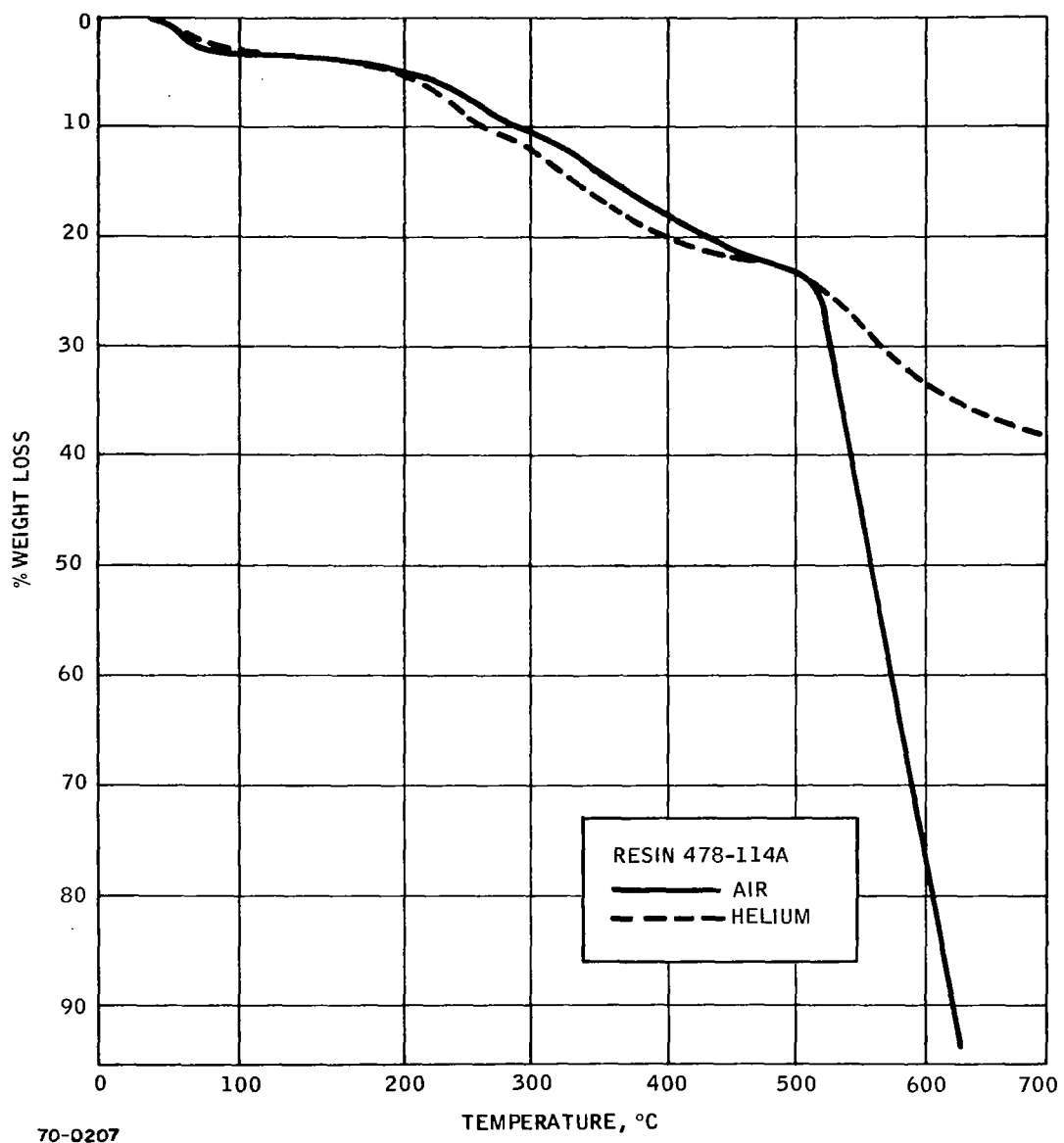
Figure 11 COMPARISON OF WEIGHT LOSS IN AIR AND HELIUM IN TGA APPARATUS FOR
MIXED OLIGOMERS

70-0207

18

WEIGHT LOSS, %

TEMPERATURE, °C

SAMPLE NO.	478-126A	478-126C	478-130A
pH	1.5 - 2.0	4.5	1.5 - 2.0
SAMPLE FORM	POWDER	POWDER	POWDER
HEATING RATE	5 °C/min.	5 °C/min.	5 °C/min.
HEATING RANGE	25-700 °C	25-700 °C	25-700°C
ATMOSPHERE	AIR	AIR	AIR
FLOW RATE	1 CFH	1 CFH	1 CFH

70-0202
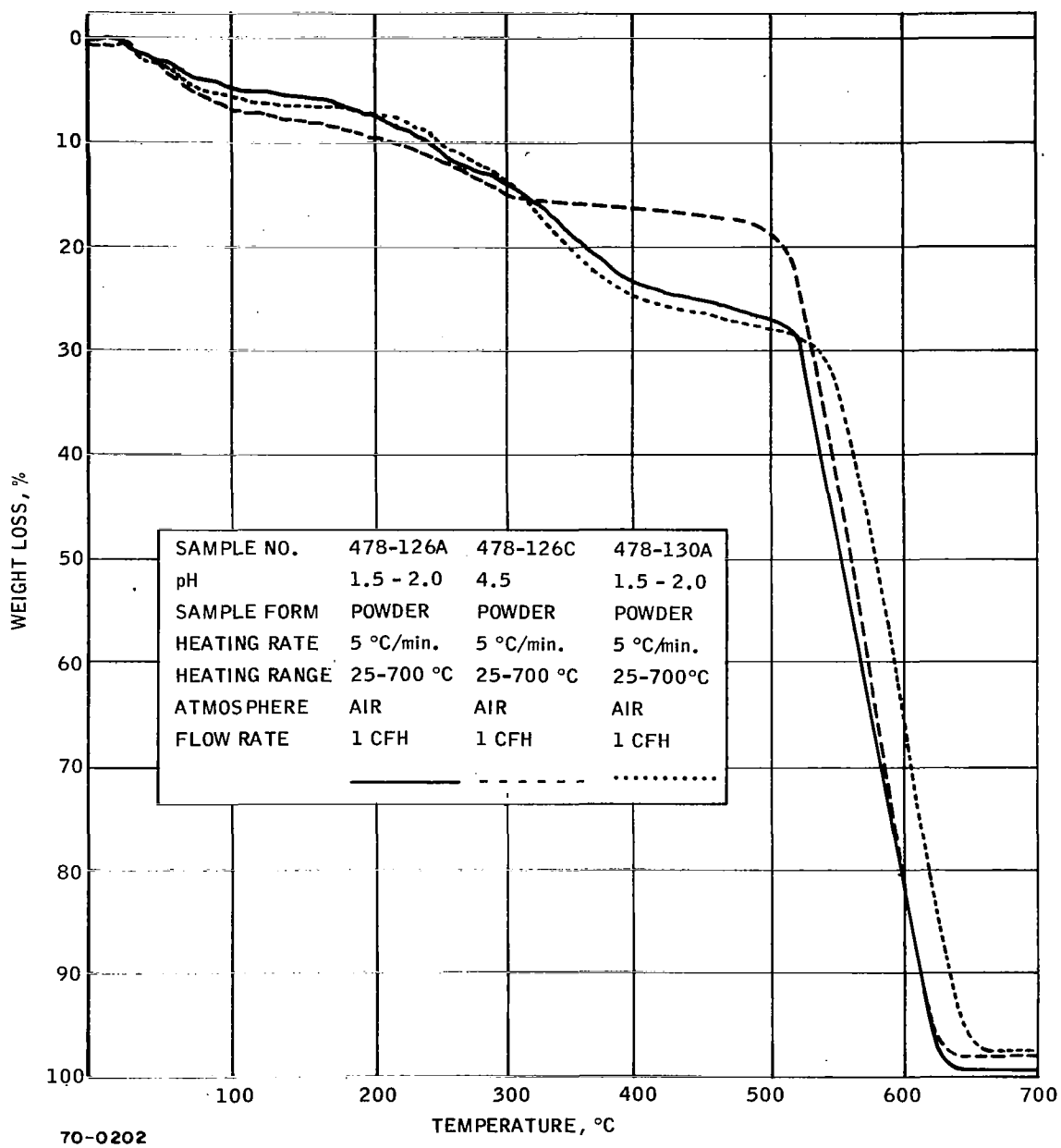
Figure 12 EFFECT OF OLIGOMER MIXTURE pH LEVEL ON TGA THERMAL STABILITY

19

The use of BSA as a solvent in the molecular mixing and/or synthesis introduced problems as well as apparently solving some. Although BSA is monofunctional and therefore cannot normally be involved in the main chain backbone, it can react with the amine end groups to stop chain growth, or react with amine along the chain to form short branches. Furthermore it can act as a plasticizer if it remains in the molding powder even without direct chemical bonding to the oligomers or polymer chains. While washing with water and/or benzene was expected to remove it completely from the resin powder, tests were performed to determine the overall neutrality of the BSA as a solvent and insure its complete removal during resin workup if that were most desirable.

The initial tests were sulfur determinations which indicated that extensive washing could give sulfur free oligomer mixtures as shown in Table V. The first three are molecularly mixed powders (Experiment 478-70 and Experiment 478-71 mixed in BSA) precipitated in water and then washed to free them of BSA by the methods described in the table. The next five are moldings made from molding powder given similar processing. The molding cycle does not result in any significant loss of sulfur that exists in the molding power as shown by the sulfur levels in CH-146 and CH-147. A comparison of CH-137 with 1022-1 and 1022-2 indicates that insufficient washing even with water leaves enough BSA behind to give a positive determination. However adequate washing can give "sulfur free" resin powder, although this powder may not be completely sulfur free since the limit of sensitivity of the sulfur apparatus is about 0.1 percent. The sulfur test for this kind of organic material with high thermal stability gave troubles since furnace temperature, catalyst concentrations and combustion times that gave good reproducibility with inorganic standards gave poor results with organic standards. Thus when a correlation of zero sulfur with pH levels in the wash water above 4.5 was uncovered further chemical sulfur determinations were not made and the more rapid determination of pH values were substituted for control purposes.

Initial moldings were made from powders produced by grinding together the dried oligomer powders in either a mortar and pestle or a ball mill. The mixed oligomers would have to have some flow to obtain good densification and enough chemical reaction must take place in the mixture to give a high polymer from the oligomer molecules. Further, the flow or viscosity of the oligomer mixture was expected to be in a tug-of-war between a rising temperature acting to decrease it and the chemical reaction of chain extension acting to increase it. However, if these parameters are to be controlled effectively then the mixing must produce intimate contacts between the oligomer end groups with minimal fluctuation in concentration throughout the powder. The effect of the oligomer mixing methods is shown in Table VI.

20

TABLE V

DEGREE OF BSA REMOVAL AS A FUNCTION OF WASHING METHOD

Material Designation	Washing Procedure	% Sulfur
478-70	10 washes with water (about 4X water volume/wash)	none
1022-1	precipitate H_2O; extract w/benzene; extract 10 days w/H_2O	none
1022-2	precipitate H_2O; extract w/benzene; extract 10 days w/H_2O	none
CH-137	6 washes with water (4X water volume/wash)	0.52
478-98	precipitate H_2O, extract acetone 5 days and 1 day H_2O	1.43
478-112	extract benzene 5 days and 1 day H_2O	5.25
CH-146	extract benzene 5 days and 1 day H_2O	5.5
CH-147	extract benzene 5 days and 1 day H_2O	5.5

TABLE VI

COMPRESSION MOLDED DISKS OF PYRRONE OLIGOMERS AFTER MIXING BY DIFFERENT METHODS

Molding Number	Method of Mixing	Temp. °F (°K)	Press Psi	Time Min.	Diameter in.	Weight Loss in Molding Percent	Specific Gravity
CH-135	None–Amine oligomer only	700(644)	1,000	60	.5 (12.7)	3.1	1.26
CH-136	None–Anhydride oligomer only	500(588)[1]	---	---	.5 (12.7)	---	---
CH-123A	Mortar and Pestle for 5 min.	700(644)	1,000	30	0.5 (12.7)	41.9	1.1
CH-123B	Mortar and Pestle for 5 min.	700(644)	1,000	30	1.5 (38.1)	22.5	1.12
CH-133	Mortar and Pestle for 10 min.	700(644)	1,000	60	1.5 (38.1)	12.8	1.14
CH-134	"	700(644)	5,000	60	1.5 (38.1)	19.1	1.27
CH-128	"	750(672)	5,000	60	1.5 (38.1)	17.6	1.28
CH-130	Ball mill for 48 hours	750(672)	1,000	60	1.5 (38.1)	17.2	1.07
CH-131	Ball mill for 48 hours	750(672)	5,000	60	1.5 (38.1)	15.9	1.29
CH-137	Benzene Sulfonic Acid, 298°F (418°K)	700(644)	1,000	60	.5 (12.7)	17.4	1.37

Note: Moldings made from mixed 478-70 and 478-71 oligomers which had been recyclized under vacuum for three hours at 410°F (483°K) except CH-123A and CH-123B which were made from 478-70 and 478-54 uncyclized.

[1] Oligomer foamed and prevented completion of molding cycle

All the initial moldings except CH-137 were made by grinding dry the correct weight of the anhydride and amine components and loading into a mold preheated to 500°F. The mold was closed with contact pressure for 5 minutes and then breathed. The mold was closed, pressured to the final molding pressure, heated to 700°F and held at that temperature for 1 hour. All of the moldings were brittle to some degree though only two moldings were fragile. Enough flow was exhibited by all the combinations tried so that no sample appeared to be just compressed spheres or powder but very little or no flash was observed. However, none of the moldings gave a fracture surface that looked homogeneous under 60X microscopic examination. Sample CH-123A which was mixed rather crudely showed black striations of a glossy nature interspersed with thin light brown streaks of a granular or foamy nature and was the least homogeneous. Sample CH-128 appeared almost uniformly black in color (very dark red in thin sections) but with indications that there were small pockets of material different from the relatively uniform matrix.

The weight loss from the molding process was generally much higher than expected. For example, with both components fully cyclized DP-1-1/2 the weight loss should be 5.3 percent and with both in the imide form at DP-1-1/2 the weight loss should be only 10.0 percent. The value observed for sample CH-127 is the only one close to the theoretical (9.1 percent actual versa 7.7 percent theoretical for 1 imide and 1 pyrrone both DP-1-1/2). Unremoved solvent and/or degradation or volatilization of oligomer that has not taken part in the solid state reaction may be the source of this discrepancy. Although the first three moldings were hardly optimized with regard to mixing, TGA curves appeared to have the major knee above 500°C. The weight loss at 315°C (600°F) ranged from 14 percent to 42 percent. This difference may well be an artifact or tied in with the molecular scale heterogeneity resulting from the crude mixing.

The moldings listed in Table VI were molded from the nominal DP-1-1/2 pyrrone materials at two different pressures. Moldings CH-130 and CH-131 (ball milled for 48 hours) were run at 750°F in the hope that better mixing and flow might occur. Although the cross sections of these two looked homogeneous in color both were very brittle and CH-130 appeared to have numerous voids accounting for its low density. The second pair mixed with mortar and pestle (CH-133 and CH-134) were molded at 700°F and were less brittle but much more heterogeneous in appearance. In each case the 5,000 psi pressure gave a significantly higher density. Each oligomer was also molded separately and although each showed flow the amine capped material required exceptionally large amounts of breathing (almost continuous) to maintain constant pressure in the mold despite the low weight loss. During this breathing cycle the button (amine capped oligomer) being molded broke in two but healed itself during the final pressurization at 700°F. The anhydride capped material foamed badly at 550°F and caused mold separation preventing further processing. This phenomenon may be due to loss of CO_2 or CO from the anhydride moiety at this temperature.

Further attempts at mechanically mixing the oligomers were dropped when it was found that benzene sulfonic acid (BSA) dissolved the cyclized oligomers completely. Each oligomer was dissolved separately in BSA heated to 100°C, mixed, and the mixture heated further to 145°C before precipitation in water. The precipitate was washed with distilled water to a neutral pH and gave about 80 percent yield. No significant increase in solution viscosity was observed during the heating cycle. However, the IR spectra of the mixed oligomers (Fig. 13 a) showed the more featureless spectra of a polymeric system which would indicate some chain extension. The precipitate was molded to 700°F at only 1,000 psi pressure (CH-137) and gave a molding with the very high specific gravity of 1.37. Equally important, the sample required very significant pressure to fracture and appeared homogeneous in both color and texture. The IR spectra of the molded piece (Figure 13 b) showed some significant differences over the precipitated mixture. In particular the molding shows a band centered about 1745 cm^{-1} that the mixture does not have, the peak at 1600 cm^{-1} is substantially stronger in the molded material and the imide band at 720 cm^{-1} seen in the mixture is either nonexistent in the molding or shifted to the region of 690 cm^{-1}. The latter is possible since there is no longer a pure imide ring if cyclization is complete.

The same molding powder, Experiments 19C3-210 and 20C3-210 oligomers molecularly mixed in BSA, was molded next in a 5 X 1 in. bar mold (CH-139). Inadvertently, the molding cycle was not that for CH-137 which had been the highest density molding to date. The molding cycle started lower and the heating was less rapid as shown in Table VII. This combination of lower initial temperature and longer time at temperature (slower heating rate) would be expected to increase the rate of chain extension and thus chain stiffness faster than the rising temperature can increase flow. Although the higher pressure should work in the opposite direction, apparently it could not compensate and the lower density resulted along with a definitely heterogeneous appearance in fracture cross sections. The molding cracked during processing but the cracks were randome and not typical shrinkage cracks. Several large pieces (up to 1 in. x 1-1/2 in. x 1/8 in.) were squared off with a diamond saw blade and tested in flexure at room temperature, 500°F, 700°F, and 1000°F. The results are shown in Table VIII. The most striking point is that this molding maintains strength and modulus effectively unchanged out to 700°F. Furthermore, the CH-139 did not fail of its own volition even at 1000°F although it did fail at no load. Portions of the sample surface remained smooth and uncracked even after a 45 min. heating cycle from 600°F to 1000°F. The fracture surfaces for this sample did not show any significant porosity even at 100X magnification. The rest of the surface showed dried mud type cracks which appeared to reach a maximum of 1/64 in. below the surface. Thus, although the sample CH-139 was of less than optimum on density and appearance, its retention of strength and modulus to high temperatures was good.

The initial synthesis work demonstrated that the oligomer route works in terms of producing a soluble product (albeit in benzene sulfonic acid) with indications from IR spectra that a significant portion of the internal structure is cyclized to the Pyrrone form. Furthermore, the molding powder

13(a)

13(b)

2000 1900 1800 1700 1600 1500 1400 1300 1200 1100 1000 900 800 700

FREQUENCY, (CM^{-1})

70-0209
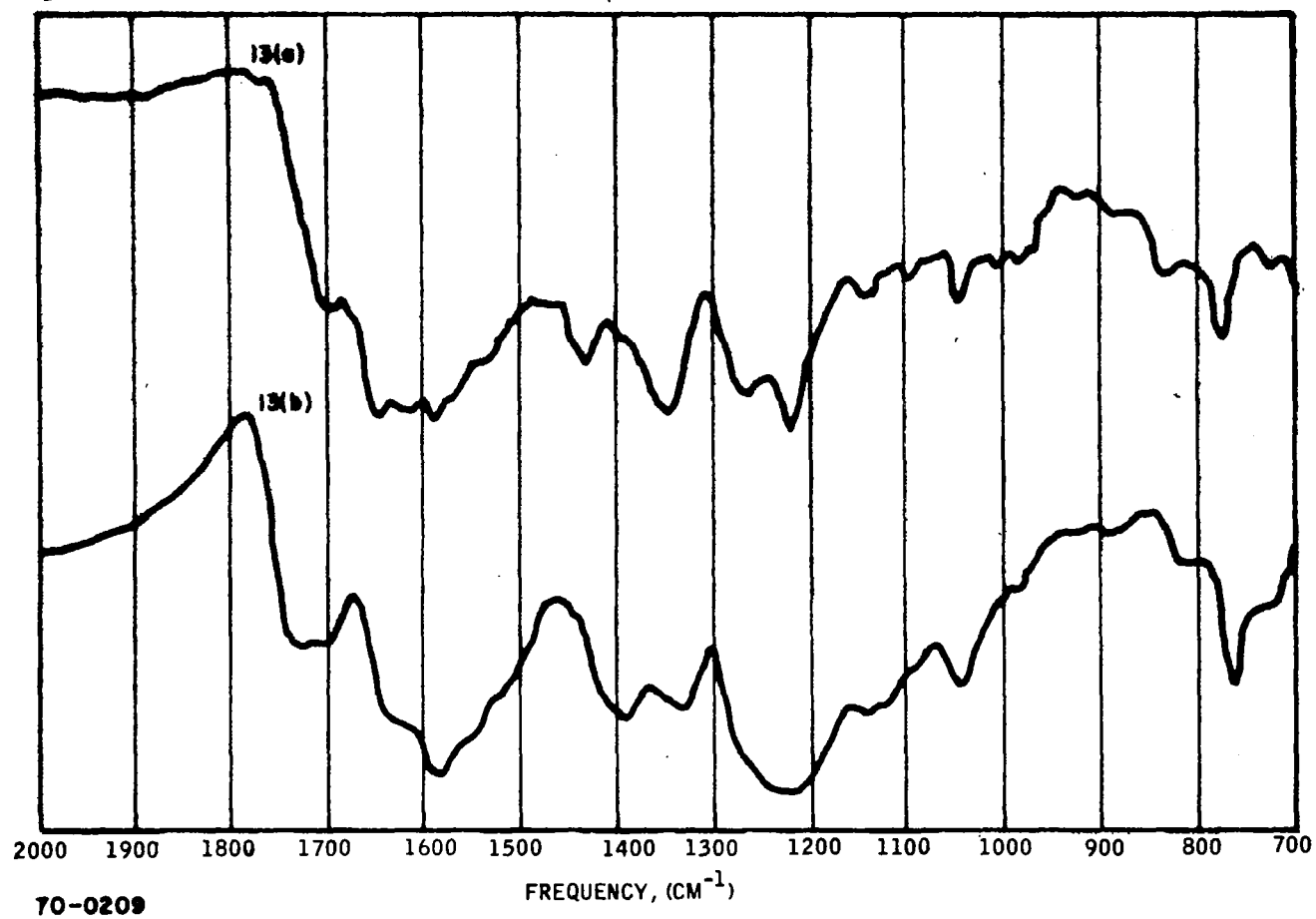
Figure 13 COMPARISON OF IR SPECTRA OF MIXED PYRRONE OLIGOMERS BEFORE (a) AND
AFTER (b) MOLDING TO 700°F

25

TABLE VII

INITIAL MOLDINGS FROM RESIN MOLECULARLY MIXED IN BSA

Sample	Initial Temperature	Final Temperature	T. Min.	Max. Press. Psi.	Time at Max. Press. Min.
CH-137	500°F	700°F	45 min.	1000	60
CH-139	400°F	700°F	100 min.	2000	60

	% Wt.Loss on Molding	ρ	Specimen	Dimensions	Barcol Hardness
CH-137	17.4	1.37	disk	0.5" dia. x 0.141" thick	92
CH-139	18.9	1.26	bar	5" x 1" x 0.118" thick	

Note: The anhydride capped oligomer was 19C3-210 and the amine capped oligomer was 20C3-210 in both cases. The oligomers were dissolved separately in benzene sulfonic acid (BSA) mixed, precipitated in water, washed with water to neutral pH and dried before molding.

TABLE VIII

FLEXURAL PROPERTIES OF MOLDING CH-139

Test Temperature °F (°K)	Strength Psi	Modulus Psi
75 (297)	6,000[a]	5.1 x 10^5
500 (533)	6,100	4.6
700 (644)	5,700	5.1
1,000 (811)	0[b]	0[b]

[a]Span-to-depth ratio,   6 for 0.75 in. (19.1 mm) span

[b]Specimen was thermoplastic

Note: All the samples were held at the test temperature for 15
minutes prior to loading except the 1000°F sample. The
1000°F sample was placed in the constant temperature
chamber at 600°F and was kept in the chamber as it was
heated to 1000°F which took 45 minutes. Because of the
slow heating rate, further soaking to reach temperature
did not appear necessary and it was loaded right away.

resulting from the synthesis molds to a high density material with good thermal stability and moderately good high temperature flexural properties. This level of worth was shown in spite of a very minimal study of the molding peculiarities and critical parameters associated with this new material.

III. PRELIMINARY MOLDINGS

        After the first moldings from the initial synthesis portion of
the work showed that the mixed oligomers had enough flow to mold, a
much more ambitious molding study began. This study was purposely
made extremely wide ranging in its scope. By looking at as many
parameters as possible from the synthesis, polymer work up, molding
and post handling areas, we felt that all or most of the critical
parameters for optimum molding of the oligomer moldings powder would
be known for future use in molding process experimental design.

        The synthesis level was scaled up from approximately 100 grams to
500-750 grams. These syntheses were made varying the synthesis
parameters of monomer mole ratio in the oligomer synthesis, heating
time, and monomer addition time as shown in Table IX. The large scale
($\sim$ 1#) synthesis runs were made successfully in glass equipment. In
these runs, the amine capped and anhydride capped oligomers were
molecularly mixed directly from the synthesis reactors without inter-
mediate precipitation, washing and drying. The mixture of oligomer
solutions was precipitated within 5-10 min. of the addition of the
anhydride capped oligomer solution to the amine capped oligomer solution.
These runs were made at slightly higher concentrations and double the
amount of reactants so that slightly more than one pound of polymer with
the indicated stoichiometry was the theoretical result. The majority
of the water of hydration was removed from the BSA by vacuum distillation
(10-30 mm Hg and temperature not higher than 120°C so little or no
degradation of BSA occurs) prior to solution of the monomers. The solution
of monomers was done at temperatures between 100-150°C, the reaction was
started when both monomer solutions were at 200°C and addition took about
20-25 min. The amine-capped oligomer was made first since it is less
susceptible to branching. The equipment was rinsed out with BSA and the
anhydride synthesis started immediately. The hot (200°C) anhydride
oligomer solution was poured into the amine oligomer solution (tempera-
ture 100°C) with vigorous stirring which was continued for about 5 minutes
the addition was complete. The mixed solutions were then siphoned through
Teflon tubing into about three times their volume of room temperature
distilled water. The water was stirred very vigorously with an air motor
and stainless steel propeller. The yellow suspension was allowed to settle
and most of the light yellow liquid decanted off in preparation for further
washing. Polymer recovery was generally better than 70 percent of
theoretical with this synthesis technique.

        During the initial molding work with powders molecularly mixed in
BSA some moldings were made in which unexpectedly large flow was observed.
A mold loaded with enough powder to give a 130 mil thick piece gave
instead a 10 mil thick sample and large amounts of flash. Since the BSA
is not a volatile solvent and must be extracted from the molding powder
it was suspected as a plasticizer. Several moldings were made therefore
of different sulfur levels to look at the removal requirements of the BSA.
The various sulfur levels were obtained by washing the mixed oligomer
powders to various pH levels. Data on the molding characteristics of
these materials are given in Table X.

TABLE IX

VARIATION IN SYNTHESIS PARAMETERS FOR PRELIMINARY MOLDING STUDIES

Exp. #	End Cap	Mole Ratio	Conc.	Synthesis Temp.	Time in Pot	Time for Addition	Wt. of Both Monomers	Molecular Mixing Time	Color of Product
478-114	Amine	2:1	0.25M/0.3M	200°C	1 hr.	40 min.	225.0 gms.	10 min.	light
	Anhydr.	2:1	0.25M/0.3M	200°C	1 hr.	20 min.	257.0 gms.		yellow
478-116	Amine	2.2:1	0.25M/0.3M	200°C	1 hr.	10 min.	237.9 gms.	15 min.	light
	Anhydr.	2:1	0.25M/0.3M	200°C	1 hr.	15 min.	257.0 gms.		yellow
478-118	Amine	2:1	0.25M/0.3M	200°C	45 min.	20 min.	225.0 gms.	15 min.	light
	Anhydr.	2.2:1	0.25M/0.3M	200°C	45 min.	20 min.	277.2 gms		yellow
478-120	Amine	2:1	0.25M/0.3M	200°C	30 min.	25 min.	225 gms.	15 min.	light
	Anhydr.	2:1	0.25M/0.3M	200°C	25 min.	20 min.	257 gms.		yellow
478-122	Amine	2.25:1	0.25M/0.3M	200°C	25 min.	20 min.	241.1 gms.	15 min.	light
	Anhydr.	2.25:1	0.25M/0.3M	200°C	25 min.	20 min.	281.2 gms.		yellow
478-135	Amine	2:1	0.25M	200°C		5 min.	450 gms.	30 min.	red-
	Anhydr.	2.2:1	0.25M	200°C		6 min.	553 gms.		brown

TABLE X

EFFECT OF RESIDUAL SULFUR CONTENT ON MOLDING BEHAVIOR OF MOLECULARLY MIXED PYRRONE OLIGOMER

Molding Number	Residual Sulfur Percent	Molding Conditions				Wt.Loss in Molding Percent	Specific Gravity	Remarks
		Initial Temp. °F(°K)	Final Temp. °F(°K)	Press Psi	Time Min.			
1022-1	0	500(533)	700(644)	1,000	30	13.6	0.94	Very little flow
1022-2	0	640(611)	750(672)	5,000 8,000	30	11.3	1.11	Preform made at room temperature, 30,000 psi, 5 min.
CH-139	0.5	400(477)	700(644)	1,000	60	18.9	1.26	Satisfactory molding; used for flexural tests
1022-3[1]	1.3	500(533)	700(672)	5,000	30	10.7	1.30[2]	Low to moderate flow; sample wedge shaped
CH-146	5.5	500(533)	700(672)	1,000	—	----	----	Excess flow
CH-147	5.5	500(533)	700(672)	1,000- 8,000[3]	135	----	----	Self induced pressure increase

Note: All moldings except 1022-3 made from mixed 478-70 and 478-71 oligomer which had been cyclized under vacuum for three to six hours at 410°F (483°K)

[1] Made from resin 478-114 which was made and mixed in BSA solution

[2] Molding heterogeneous in color; specific gravity of thicker dark portion 1.38

[3] Most of pressure rise self induced

CH-139 had 0.52 percent sulfur while the repeat mixture from
Experiment 19 and 20 was extracted initially with benzene and then
only for a short time with water. The result (CH-146) was massive
flow that ended with almost no polymer in the mold. A repeat molding
(CH-147) with longer times at the lower temperatures, lower pressures
to start and more breathing also gave substantial flow but was much
more contained although there was a large self-induced pressure build-
up by the volatiles trying to escape. The powder was then extracted
with water for 8 more days at which point no sulfur could be detected.
Moldings 1022-1 and 1022-2 were then made with this completely extracted
resin. No flow was observed and very little flash and the moldings
had very low densities. The last data are from resin made and mixed in
BSA (without precipitation of oligomers) and washed to $\sim$ 1.3 percent
sulfur. Although the piece was heterogeneous and wedge shaped, the
overall density was high (1.30) and the density of the thicker blackish-
brown portion was the highest yet (1.38). The implication from these
results is that the BSA maybe acting as a fugitive plasticizer during
molding and that it either reacts eventually or degrades and goes off
as a gas (benzene and SO_2). It was speculated at this time that the
modulus retention at high temperatures may be due to sulfone crosslinks
from the BSA. Later data in which even higher moduli were obtained
with molding powder that was sulfur free indicated that such crosslinking
was not a major factor even if it occurred. However, it was evident
that the low pH, high sulfur content powder flowed more readily during
molding than did the high pH, low sulfur content powder.

The effect of overall stoichiometry for resin washed to a low pH
is shown in Table XI. All of the samples were preformed and then post-
cured i.e, fabricated without press molding. There is very little
difference in the final specific gravity which is the noraml range for
samples postcured to 850°F and reflects the similar narrow range of
specific gravities at the preform stage. The relatively constant
modulus values at both 500 and 900°F indicates that there is little
difference in the degree of cyclization in the cured moldings regardless
of stoichiometry from excess anhydride through the balance point to the
excess amine side even at 900°F. By contrast the strength values indicate
that off-stoichiometry in either direction is better than the balanced
ratio. One can speculate that the chain extension process is hampered
by the lack of high temperature curing under pressure and this is supported
by the low strength values at 500°F shown by all the samples. If this be
true then the off-stoichiometry samples which should have more branching
and more tendency to cross link could exhibit higher strength due to
increased chain entanglement and/or crosslinking. The cross linking
reaction would result in a strength mechanism that is less temperature
dependent and therefore should show increased properties at 900°F, as
is indeed the case. In fact, the strength values at 900°F, for the off
stoichiometry resins are among the highest ten values observed throughout
the program.

TABLE XI

EFFECT OF RESIN STOICHIOMETRY ON HIGH TEMPERATURE FLEXURAL PROPERTIES

| Sample # | Resin | pH | Monomer Ratios | | Preforming Conditions | | Post-cure Temp °F | Specific Gravity | Strength | | Modulus | |
			Oligomer Amine Capped Anhydr. Capped	Overall Anhydr. to Amine	Temp.	Press			500°F psi	900°F psi	500°F psi x 10^{-6}	900°F psi x 10^{-6}
1022-31	478-114A	1.5	2:1 1:2	1:1	300°F	60	850	1.23	3700	2550	0.39	0.25
1022-38	478-114A	1.5	2:1 1:2	1:1	350°F	60	850	1.25	3660	2300	0.50	0.26
1022-28-I	478-116A	1.5	2.2:1 1:2	1:1.07	300	60	850	1.22	4370	4050	0.35	0.25
1022-24-A	478-118A	1.5	2:1 1:2.2	1.07:1	300	60	850	1.23	5190	6560	0.36	0.31

The washing procedure used to remove the BSA solvent requires that the resin be extracted with large quantities of water. Although the amine monomer is only slightly soluble in cold water enough of the unreacted amine monomer could be extracted to upset the overall stoichiometry intended for the run. To investigate whether the stoichiometry is inadvertently being changed this way, a small portion of resin 478-138 (Experiments 51 and 52) was molecularly mixed in two separate ways in an attempt to determine the best ratio of the oligomers for molecular mixing. In the first, equal moles (equal volumes since concentrations in each oligomer synthesis were the same) of anhydride capped oligomer and amine capped oligomer were heated separately to 170°C and poured together with very vigorous stirring. The viscosity of this mixture was then read with a Brookfield viscometer. The second method involved heating unequal moles separately to 170°C, then mixing with vigorous stirring and reading the viscosity. This mixture was then brought step by step through the 1:1 stoichiometry point in small increments with the viscosity read after each addition. The viscosity of the mixture from the first method was identical to that obtained at the 1:1 stoichiometry point by the second method. Two peaks in the viscosity-stoichiometry curve at the high anhydride imply the existence of more than one reaction occurring and may be tied in with branching and cross-linking. Materials from each of these mixtures were precipitated and washed to a pH of 3-3.5 and dried.

Two moldings were made from resin solution titrated slowly to the 1:1 overall stoichiometry and two from resin from the standard method of pouring the anhydride capped oligomer solution as rapidly as possible into the amine capped oligomer solution. Both solutions were heated at 170°C before precipitating in water and washing to a pH of ~ 4.5. The flexural test results of the moldings (Table XII) show no significant difference between the molecular mixing procedures. The titrated mixing mode shows higher strength and modulus at the lower temperatures but only the strength difference at 700°F is large enough to be significant. The overall molding specific gravities are very low which can account for the generally low values and may have prevented a correlation from being seen. The strength values in the data which appear high relative to the rest of the set were checked carefully and are most likely a result of the test pieces having fewer flaws or noncritical flaws.

The effect of the more conventional molding parameters such as pressure during molding and molding temperature are shown in Tables XIII and XIV respectively. Pressure changes from 5,000 to 30,000 psi do not appear to show any significant difference in flexural properties but the specific gravity difference is probably significant. Attempts at correlating large quantities of data especially in the pressure range of 1000-10,000 gave negative results. The data shown in Table XIV are the average of three to nineteen mechanical test values taken regardless of other parameter variations. Such correlations as might be seen should be used with caution and were used only in defining parameters for the molding process experimental design. The 800 and 820°F data had the smallest population and are therefore the most subject to error or to be bothered by artifact. The general trend to the data is that higher molding temperatures tend to increase higher temperature strength and modulus.

TABLE XII

EFFECT OF MOLECULAR MIXING TECHNIQUE ON FLEXURAL PROPERTIES

Test Temperature	Resin / Flexural Property	478-139 -170 BM	478-139 -170 BT
500°	Sb $E \times 10^{-6}$	5500 0.41	7100 0.51
700°	Sb $E \times 10^{-6}$	6000 0.39	10,900 0.45
800°	Sb $E \times 10^{-6}$	6700 0.21	8000 0.30
900°	Sb $E \times 10^{-6}$	5200 0.23	3600 0.21
1000°	Sb $E \times 10^{-6}$	2100 0.10	1750 0.11
Molding Specific Gravity		1.18	1.23

478-139-170BM   Standard single addition molecular mixing

478-139-170BT   Titrated multiple addition molecular mixing

35

TABLE XIII

EFFECT OF MOLDING PRESSURE ON FLEXURAL PROPERTIES

Sample #	Molding Pressure psi	Specific Gravity	Flexural Properties		Test Temp. °F (°K)
			Strength psi	Modulus psi x 10^{-6}	
1028-118	5,000	1.32	12,400	0.602	500 (533)
			4,000	0.244	900 (755)
1028-125A	30,000	1.39	10,700	0.568	500 (533)
			3,300	0.173	900 (755)

Note: Both moldings were made from 1039-27 resin washed to pH 5.0, molded at 750°F for 60 minutes, and cooled to 500°F under pressure. Two plies of bleeder cloth were used above and below the molding powder during the cure cycle.

TABLE XIV

EFFECT OF MOLDING TEMPERATURE ON FLEXURAL PROPERTIES

Test Temp.

		Strength in Psi				
Molding Temp.	R.T.	500	700	800	900	1000
700	12,700	8,600	6,900	3,400	3,300	1,800
750	22,300	9,400	6,800	5,000	4,000	2,400
		4,900	5,100	5,900	5,200	2,100
		7,100	10,900	8,100	3,600	1,800

		Modulus psi x 10^{-6}				
700	0.86	0.48	0.29	0.19	0.15	0.08
750	0.82	0.44	0.31	0.28	0.25	0.14
800		0.41	0.38	0.26	0.27	0.11
820		0.52	0.45	0.31	0.21	0.12

37

One of the standard molding techniques for condensation resins is that of low-temperature preforming under vacuum. The preforming of the powder reduces the handling problems (such as spreading the powder in a hot die). The vacuum tends to remove the volatile material as it is formed thereby driving the condensation reaction toward completion. Volatile removal is facilitated further by placing one or more layers of glass fiber cloth above and below the powder to serve as an escape path. Preforms were made both with and without vacuum by applying a 20,000 psi pressure at 350°F for 30 min. The weight loss for the vacuum preforms (6.9 percent) was more than twice that for the nonvacuum preforms (3.0 percent). Unexpectedly, however, the pH 4.5 powder lost nearly twice the weight of the pH 1.5 powder for a given preform condition (vacuum or nonvacuum).

The flexural properties obtained from moldings of the pH 4.5 and pH 1.5 powder did not show as distinct a difference between the vacuum bag and nonvacuum bag preforming as did the weight loss data. The flexural test data are arranged in Table XV to emphasize the effect of the vacuum bag preforming and resin pH on the flexural properties. There is a consistent sharp drop in strength between 700 and 800° for all samples regardless of preform conditions or resin pH. A similar break in modulus values is also shown by the nonvacuum bag preformed moldings while the vacuum bag preformed moldings show a much more gradual decline with increasing temperature. In fact the pH 1.5 material shows no break in modulus out to 1000°F though the pH 4.5 material just appears to postpone the drop to the 800-900°F region. Neither strength nor modulus levels are consistently higher for vacuum bag preforming at both pH ranges. The consistently higher strength levels for nonvacuum preforming at the low pH level and for the vacuum bag preforming at the high pH level may indicate a significant interaction between the parameters.

Infrared spectra (Fig. 14) and DSC data on Cp (Fig. 15) were obtained for all four specimens 1022-73 through 1022-78, samples which compared the use of vacuum bag preforming with nonvacuum bag preforming. 1022-78 (vacuum bag preform, pH 4.5) has a spectra that is substantially different from its nonvacuum pH 4.5 molding. The imide and imidazole bands are more pronounced indicating more complete cyclization and the spectral bands are more diffuse which frequently indicates higher molecular weight. The pH 1.5 pair, 1022-73 and 1022-76, show the same trend on diffuseness but not on cyclization. The Cp data as a function of temperature, Figure 15, also show a significant difference between the vacuum bag and nonvacuum bag moldings. Both nonvacuum bag samples 1022-73 and 1022-77 indicate a reaction occurring in the 600 to 700°F region. On the other hand, for the two samples that appear to be the most fully cyclized according to IR spectra (1022-78 and 1022-73), the Cp continues to rise at 900°F. The less cyclized pair, 1022-77 and 1022-76, have a Cp curve that dips (curls down) in the 800 to 900°F region, possibly presaging an oxidation reaction.

TABLE XV

EFFECT OF VACUUM BAG PREFORMING ON HIGH TEMPERATURE FLEXURAL PROPERTIES

Molding Number	Resin pH	Preform Conditions	Strength Psi x 10^{-3}						Modulus Strength Psi x 10^{-6}						Specific Gravity of Molding
			R.T	500	700	800	900	1000°F	R.T.	500	700	800	900	1000°F	
1022-76	1.5	vacuum	10.8	8.3	11.1	2.6	2.5	2.4	0.84	0.45	0.36	0.31	0.26	0.23	1.29
1022-73	1.5	non-vacuum	17.0	12.4	11.1	3.9	3.4	2.6	0.99	0.50	0.31	0.08	0.09	0.057	1.38
1022-78	4.5	vacuum	13.1	16.6	12.6	5.7	3.3	1.4	0.98	0.59	0.22	0.17	0.07	0.02	1.32
1022-77	4.5	non-vacuum	10.1	6.0	11.2	2.3	2.1	0.8	0.61	0.45	0.23	0.06	0.05	0.03	1.22

Note: All samples were made from resin 478-126, preformed for 30 minutes at 350°F under 20,000 psi and then molded for 60 minutes at 700°F under 5000 psi.
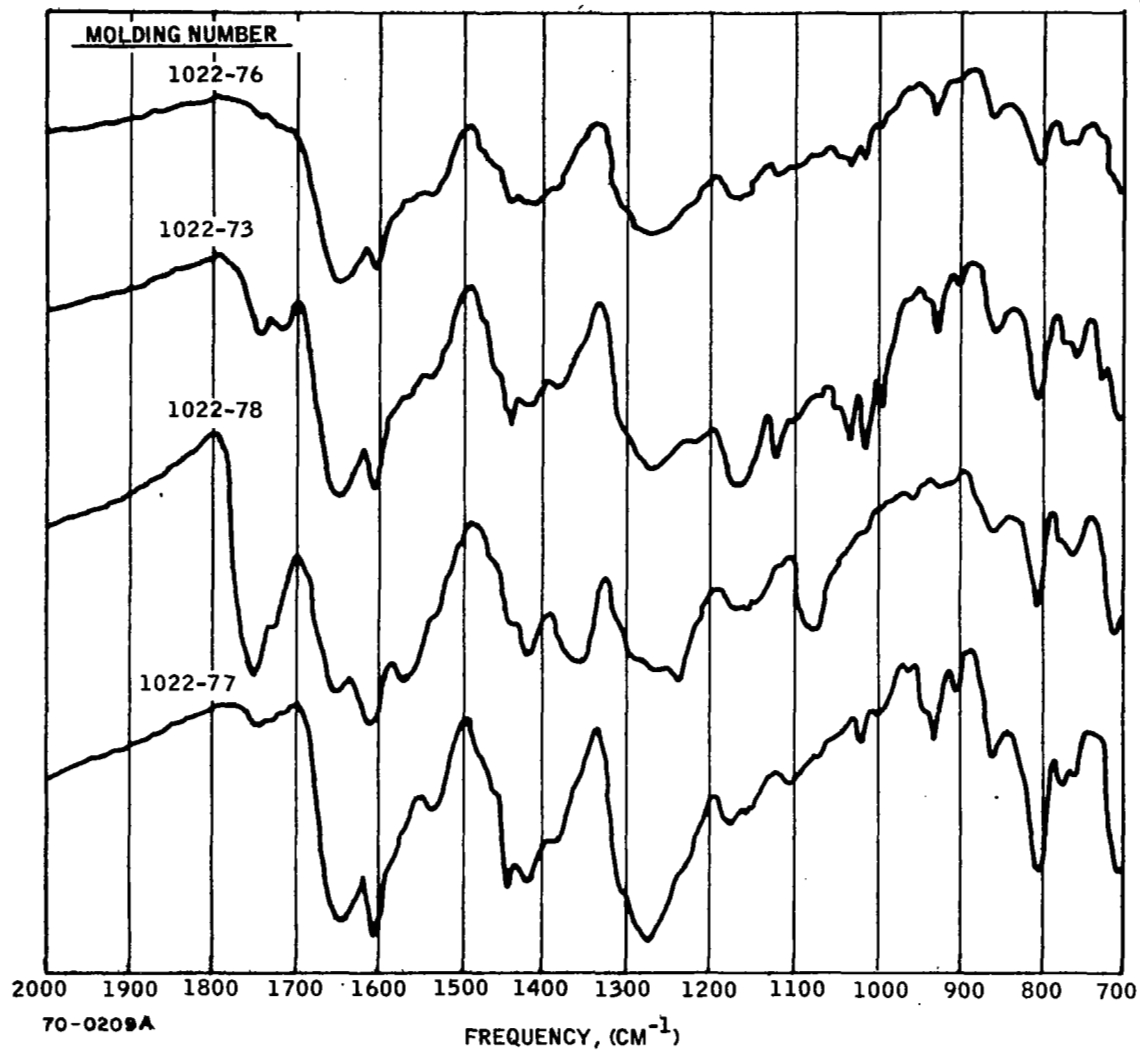
Figure 14 EFFECT OF RESIN pH AND USE OF VACUUM IN PREFORMING ON IR SPECTRA OF PYRRONE MOLDINGS

40
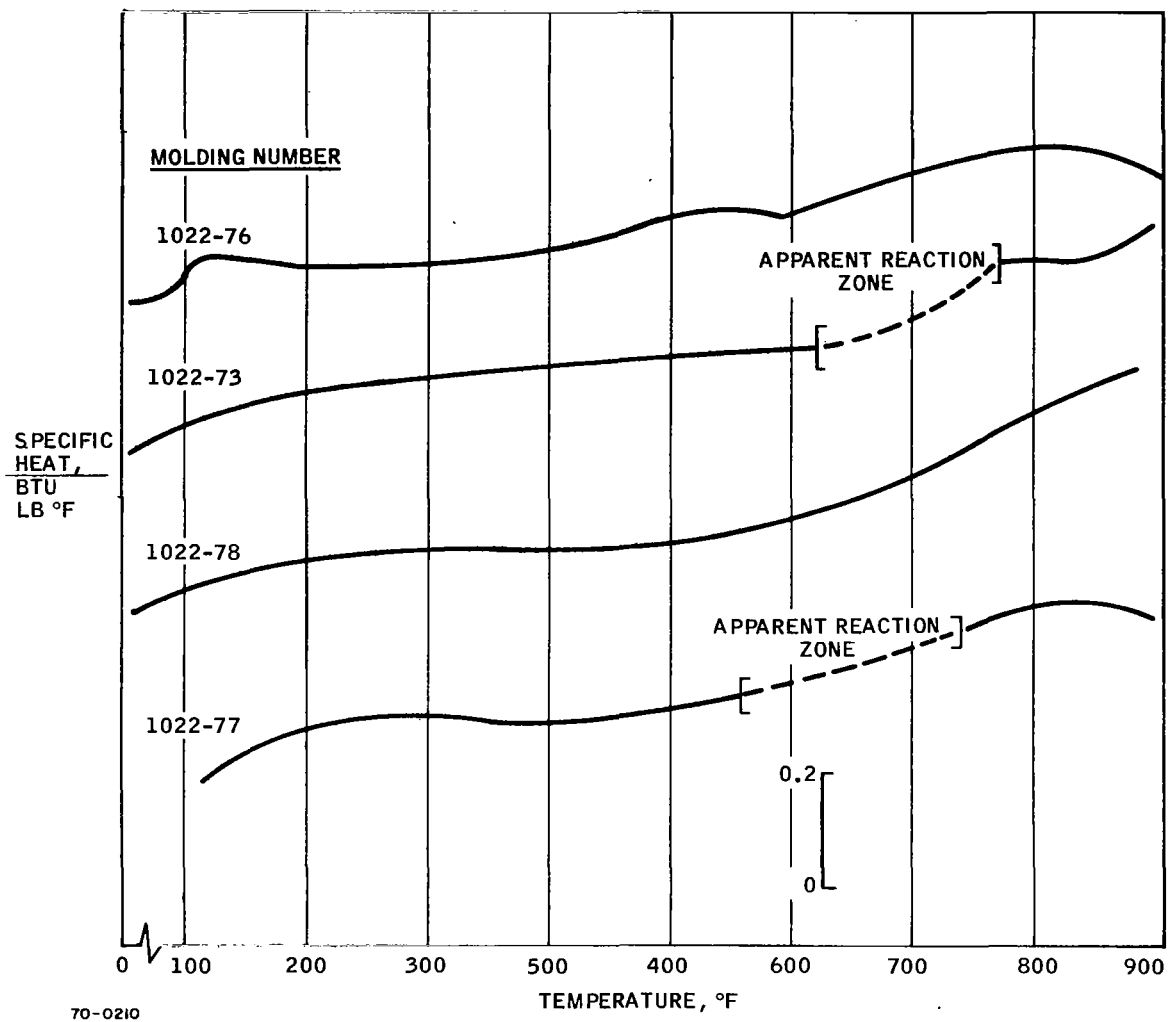
Figure 15 EFFECT OF RESIN pH AND USE OF VACUUM IN PREFORMING ON SPECIFIC HEAT OF
PYRRONE MOLDINGS

70-0210

41

Structural uses for high temperature resins are seldom restricted to short exposure time to the high temperatures. Furthermore, the majority of uses require ability to withstand oxidizing environments (generally air). Thus when the high temperature strength properties showed exceptionally high values, high temperature aging tests in air were started on a variety of moldings. The tests were made at $600^{\circ}F$ in circulating air with exposure times as long as 1000 hours. The complete data for seven early samples are shown in Figure 16. 125-6 is LRC molding powder molded at LRC; 0152 is Avco molding powder molded at LRC and the rest are Avco molding powder (various) molded at Avco under various conditions. For comparison two molded polyimide pieces (labeled Commercial 1 and 2) were also aged under the same conditions. The dotted line portions are estimated data for weekends when daily weighings were not made. Weight loss of the pyrrone samples at 150 and 200 hours is listed in Table XVI in order of increasing weight loss of all pyrrone samples that have been aged. The only apparent correlation between the weight loss data and molding parameters (also listed in Table XVI) is with the absence or presence of bleeder cloth. Note that 6 out of the bottom 7 were molded without bleeder cloth. The chances of picking the order of the first 7 at random from seven no's and 7 yeses is about 1 in 500.

Both moldings 1022-77 and 1022-78 were made from high pH material with -78 vacuum bag preformed and -77 not. The very low oxidation rate compared to the conventional route pyrrone (125-6) may be an indication that the oligomer route more nearly approaches the pure pyrrone structure and thus would indicate more nearly the potential of this structure.

The four moldings that were made to look at the effect of molecular mixing mode were also tested for oxidation resistance. After 168 hours at $600^{\circ}F$, the titrated samples had lost more than twice as much weight (23 percent) as the rapid mix samples (10 percent). However, neither weight loss value was especially low. A later investigation indicated that the oligomer mixing temperature ($170^{\circ}C$) may have been the reason for the high weight loss of the samples. The last set of aging data was done on samples cut from an 8-1/2 in. x 2-1/4 in. plate (1028-90). These samples had about one-sixth the mass of the samples which are listed in Table XVI. The average weight loss of eighteen samples at $600^{\circ}F$ in air was: 5 percent after 250 hours, 11 percent after 500 hours, 19 percent after 750 hours, and 34 percent after 1,000 hours. These weight loss values are comparable to the lowest values plotted in Figure 16.

Weight loss from aging at high temperatures is used only as an indication of the mechanical strength retention after such aging. Flexural strength data were obtained from the aged portion of 1022-78. Table XVII shows the flexural properties of the core material before and after the aging at $600^{\circ}F$ in air. The "as cured" sample had the surface removed to eliminate the roughness from the bleeder cloth while the aged portion was cleaned to eliminate effects of the mud crack surface (1022-78 had a very thin degraded surface about 10 mils deep that had the appearance of very fine mud cracks). Six samples were machined from core material to get proper span to depth ratio and two were left full thickness to test the debilitating effect of the surface.
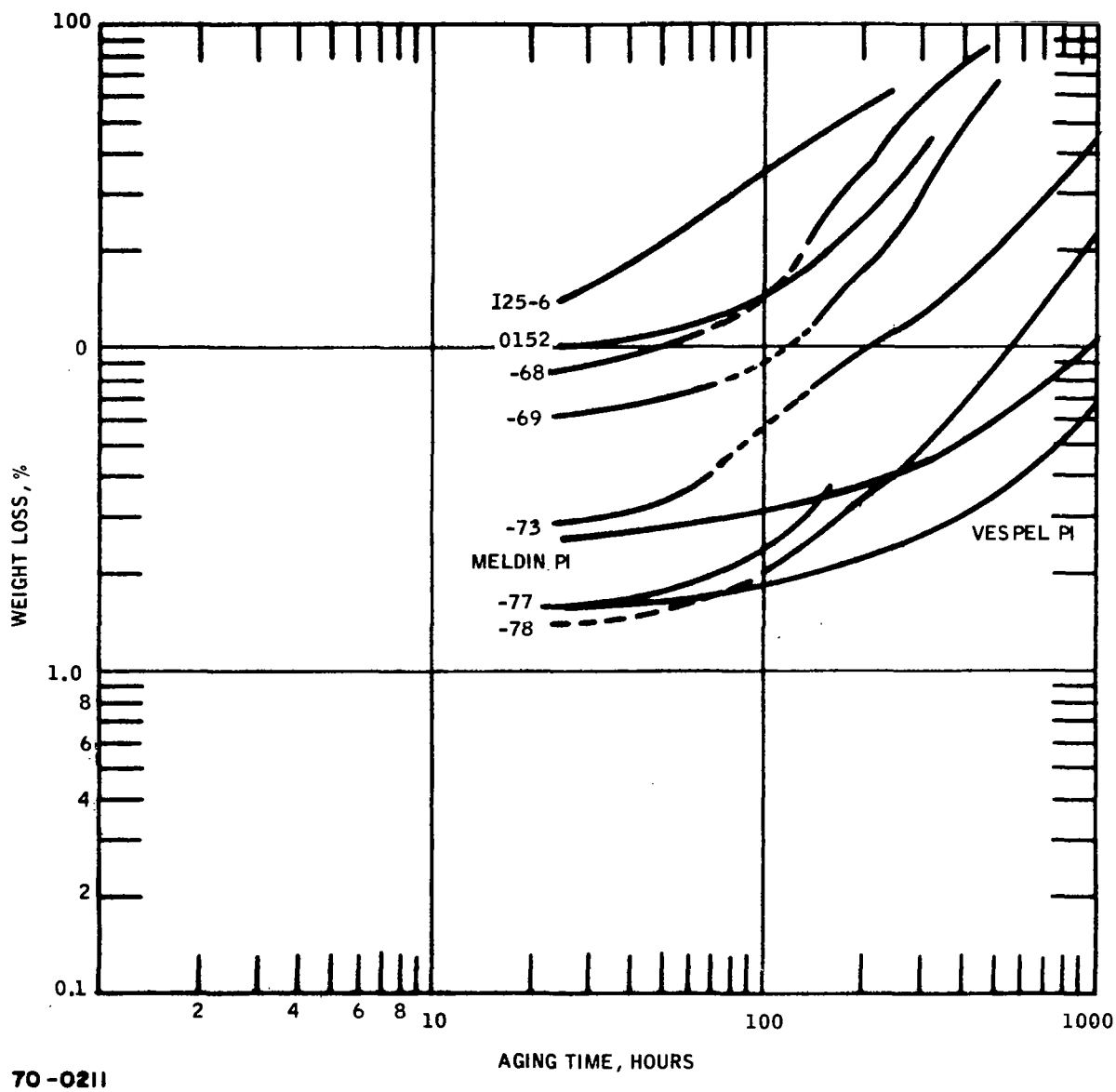
Figure 16 WEIGHT LOSS FROM AGING AT 600°F IN AIR

70-0211

44

TABLE XVI

EFFECT OF MOLDING PARAMETERS ON WEIGHT LOSS IN AGEING AT 600°F IN AIR

Sample No.	Resin pH	Molding Temp. °F	Molding Press.	Yes or No Preform	Yes or No Vac. bag	% Wt. Loss @ 200 hrs.	% Wt. Loss @ 150 hrs.	Yes or No Bleeder Cloth Molding	% Wt. Loss in Molding	Specific Gravity of Molding
1022-78	4.5	700	5,000	yes	yes	3.3	2.7	yes	14	1.30
1022-77	4.5	725	5,000	yes	no	4.4	3.4	yes	20	1.16
1022-73	1.5	700	5,000	yes	no	9.7	7.9	yes	15	1.29
1022-76	1.5	735	5,000	yes	yes	14.8	10.3	yes	20	1.21
1022-69	4.5	750	5,000	no	no	17.1	12.7	no		1.21
1022-82	3.5	715	5,000	yes	no	19.9	14.9	yes	21	1.27
1022-79	3.0	720	5,000	yes	yes	23.5	17.7	yes	18	1.28
0.152				no	no	25.2	18.4	no		
0.153				no	no	28.8	20.3	no		
1022-68	1.5	750	5,000	no	no	34.8	25	no	24	1.30
0163				no	no	43.3	30.7	no		
1022-80	3.5	715	5,000	yes	no	43.9	31.8	yes	13	1.31
125-5				no	no	54.1	42.6	no		
125-6				no	no	54.3	44.2	no		

TABLE XVII

Molding 1022-78

STRENGTH RETENTION AFTER
1000 HOURS @ 600°F IN AIR

TEST TEMP.	Flexural Strength		FULL THICK. AFTER	Flexural Modulus		FULL THICK AFTER
	BEFORE	AFTER		BEFORE	AFTER	
Room Temp.	13,100 psi	14,500 psi		0.98×10^6 psi	0.9×10^6 psi	
500°F	18,500	14,500	5,500 psi	0.73	0.57	1.71×10^6 psi
700°F	12,600	12,900		0.22	0.49	
800°F	5,700	10,100		0.17	0.40	
900°F	3,300	3,720	4,200	0.066	0.16	0.63
1000°F	1,360	1,580		0.020	0.050	

Note: All samples except those under heading "Full Thick." were core material with all surfaces ground to sound material

There appears to be no significant change in strength from the aging but the higher temperature moduli ($600°F$) have all increased. This is most likely an indication that significant postcuring had taken place and confirmed the decision to include postcuring in the experimental design. The two low span-to-depth ratio specimens were those left full thickness to test the effect of the cracked skin on flexural properties. The strength at $500°F$ is low but the strength at $900°F$ and the moduli at both temperatures are quite high. These data were checked and rechecked. Certainly a conservative comment would be that the 1,000 hours of aging did not reduce the flexural properties significantly. One must question the substantial difference in modulus between the thin and thick samples at the same temperature. Possibly the thick samples are not at thermal equilibrium when tested but the embedded thermocouple time tests done at the beginning of our testing do not support this and the softer (lower modulus) surface should tend to decrease apparent modulus and increase strength (flaws less critical). If the specific gravity were not constant but instead varied with position in a thickness direction so that it is a maximum on the surface and minimum at the center (neutral axis), then strength and modulus would change in the directions observed. However, the amount of change is unexpectedly large.

In spite of the large number of moldings made during this preliminary molding phase of the program relatively little data were obtained that could be used to define molding or resin reproducibility. Table XVIII lists seven moldings all made from anhydride rich resin. The resin came from two batches and the resin from the first batch was extracted to two different pH (sulfur) levels. Both the physical properties and the flexural properties show a wide range of values from what should be identical or very similar moldings. Specific gravities range from 1.13 to 1.33 for one pH level and from 1.12 to 1.31 for the other pH level. The mechanical properties vary just as much and range from very poor to excellent within the same sample. At least as critical from the standpoint of application is that the moldings also varied considerably in toughness. Moldings 1022-15, 1022-20, and 1022-80 showed good elongation and high strength but molding 1022-87 was very fragile and brittle.

Besides the immediate effect of obtaining an individual correlation between a molding or synthesis parameter and a physical, mechanical, or thermal property all of these studies were aimed at separating the important molding and synthesis parameters from the unimportant ones in order that a well designed experiment could be defined to study the molding process as a whole.

Based on the data from the first seventeen moldings made, a tentative design of a 2_{III}^{5-2} fractional factional was picked. This design allowed each main factor to be evaluated independently of any other main factor but the main factors would be confounded with two factor interactions.

TABLE XVIII

EFFECT OF MOLDING TO MOLDING AND RESIN BATCH VARIATIONS ON FLEXURAL PROPERTIES

Sample #	Resin	Molding Temp. °F	Molding Press. psi	Preform Temp. °F	Preform Press. kpsi	Ultimate Stress psi	Modulus E X 10^{-6} psi	Test Temp. °F	Specific Gravity
1022-15	478-118A	750	5,000			17,500	0.54	500	1.33
						6,510	0.21	700	
						2,410	0.32	800	
						7,000	0.37	900	
1022-50	478-118A	750	5,000			10,400	0.44	500	1.27
						6,140	0.41	700	
						6,530	0.28	800	
						4,280	0.21	900	
1022-20	478-118A	700	10,000	300	30	13,700	0.44	500	1.13
						9,900	0.32	700	
						5,160	0.21	800	
						6,010	0.21	900	
1022-87	478-136A	750	5,000	350	18	----	----	500	1.19
						11,200	1.69	700	
						----	----	800	
						394	0.88	900	
1022-80	478-118C	715	5,000	350	20	14,900	0.58	500	1.31
						5,600	0.43	700	
						7,400	0.36	800	
						6,400	0.35	900	
1022-51	478-118C	700	10,000	300	30	4,600	0.40	500	1.12
						1,600	0.04	700	
						500	0.01	800	
						400	0.01	900	
1022-52	478-118C	710	5,000	----	----	2,700	0.65	500	1.24
						----	----	700	
						----	----	800	
						3,200	0.13	900	

Note: The suffix on the resin number indicates resin washed to pH of 1.5 while C suffix indicates resin washed to pH 4.5

Also two factor interactions would be confounded with other two factor interactions. Other designs and various levels of the independent variables were considered but it was felt that the initial design should be uncomplicated and brief. This would provide an efficient general mapping of the region of interest and a sound basis for detailed study of critical areas. However, the initial design was abandoned when the change to BSA as solvent and further molding at even higher temperatures indicated that a wider range of variables than the 2^{5-2} design would allow would probably be necessary. As an example, the vast changes in flow observed when the BSA solvent was extracted to several different pH levels indicated that resin pH should probably be included in the design. Thus the switch to BSA as solvent forced a reexamination of the basis, factors and levels of the design. Preliminary correlations between molding parameters and the physical and mechanical properties were obtained from 35-40 moldings made by many different processes. These correlations indicated which factors were necessary to define preforming and postcuring operations as well as synthesis and molding variables. In addition the range of the final molding temperature and pressure were expanded. The molding temperature should have probably included three levels; but since that would complicate the design enormously, the temperature levels were broadened but left at two levels (700 and 800°F). The pressure level was also expanded to 1000 psi and 10,000 psi. Thus, the second stage experimental design factors considered critical with anticipated operating levels are listed in Table XIX.

TABLE XIX

CRITICAL VARIABLES FOR MOLDING PROCESS STUDY EXPERIMENTAL DESIGN

A.	Overall Resin Stoichiometry (anhydride to amine ratio)	1.04:1	1:1
B.	pH of washed molding powder	1.5	4.5
C.	Preforming temperature	$150^\circ F$	$350^\circ F$
D.	Preforming pressure	20,000 psi	60,000 psi
E.	Initial temperature of preheated mold	$300^\circ F$	$500^\circ F$
F.	Time at initial temperature	0 minutes	60 minutes
G.	Pressure at initial temperature	100 psi	10,000 psi
H.	Final molding temperature	$700^\circ F$	$800^\circ F$
I.	Final molding pressure	1,000 psi	10,000 psi
J.	Post-cure temperature, maximum	$700^\circ F$	$850^\circ F$

IV. MOLDING PROCESS EXPERIMENTAL DESIGN

The avowed purpose of research work is to obtain information and
the more information an experimenter can get per unit labor hour or per
unit dollar the more efficient he is. Statistically designed experiments
are one means available to increase research efficiency. The increased
efficiency derives from one or more of the following advantages of a
statistically designed program.

Many variables may be studied at one time making it possible to
gain an insight into their simultaneous effect on responses of interest.

Interactions between variables can be determined. This is impossible
if the more usual one-variable-at-a-time procedure is used where, in turn,
each variable is changed with all remaining variables being held constant.

Useful directions of experimentation are often indicated which can
be explored.

The experimenter can proceed sequentially, constantly adapting his
experimentation in the light of the most current information, including
that which he himself has just collected. For this purpose fractional
factorial designs act as flexible building blocks ahd have, in fact,
been successfully employed at all stages of experimentation from start
to finish. In particular, factorial designs and fractional factorial
designs are useful even at the outset of an investigation when very little
may be known about the system. Designed experimental programs are efficient
when the purpose is to screen variables – to select out of a large number
of variables those that are most important.[13,14] Because of the careful
balance and special patterning built into statistically designed experiments,
interpretation of the results is often easy.

A fractional factorial design was picked for this work based primarily
on its degree of flexibility as well as its easy manipulation and analysis.
A 2_{III}^{5-2} fractional factorial design was picked at first and then discarded as
inadequate as explained in the previous section. The design required to
investigate the significant variables was a substantially larger factorial
design of 2^9 or 512 runs. This was obviously much too large to handle.
Alternatives were to eliminate some of the listed variables and/or to do a small
enough fractional factorial design that the number of runs would be within
reason. The latter method (fractional replica) is sure to confound some effects
of interest, since there are nine main effects and 36 two-factor interactions.
On this basis, at least, a 1/8th replica would be necessary (64 runs) to get the
main effects, and all of the two-factor interactions unconfounded. Even this
level of effort appeared marginal. The maximum size design which appeared
practicable was a 32-run design, which would limit the design to a 2^5 factorial
in complete designs or a 2^{7-2} fractional design that would permit unconfounded
values for all seven main effects and 21 two-factor interactions. It was
considered imperative that the final decision on which parameters were to be
varied and the levels of these parameters be made as a consequence of mechanical
test data and not just physical data such as specific gravity. It was con-
sidered particularly important because some of the best mechanical data
obtained at that time were gotten on low density (1.19) moldings.

Since the design size had been set at thirty-two moldings, fractional factorial designs of 2_{IV}^{8-3}, 2_{IV}^{7-2} and 2_V^{6-1} were studied in some detail. The designation used indicates that the factorial designs are 2 level designs with 32 (2^5) experiments. The first number of the superscript gives the number of independent variables to be studied and the second number indicates the fraction of the full factorial while the roman subscript indicates the amount and type of confounding to be expected in the analysis. Designs of resolution III have no main effect confounded with any other main effect, but main effects are confounded with two-factor interactions and two factor interactions are confounded with one another. Resolution IV designs require that no main effect be confounded with any other main effect nor with any two-factor interaction but two factor interactions are confounded with one another. Resolution V designs require that no main effect or two-factor interaction be confounded with any other main effect or two factor interaction but two-factor interactions are confounded with three-factor interactions.

Now it is possible if one expects no interactions to study all seventeen parameters in 32 experiments. However, since several of the parameters affect flow and/or volatiles (type and amount), interactions were expected to be of some importance. Because the variability and reproducibility of our moldings were not good at this point, the 2_V^{6-1} fractional design was picked since in addition to minimum confounding, it would also have a maximum of degrees of freedom for error determination. The seventeen parameters listed in Table XX were then separated into those to be held constant and those to be varied. When the responses to be used in the design (Table XXI) were included, in the overall design considerations, it was recognized that all of the responses could be obtained from one half of a 5 in. x 1 in. molding. Thus, postcure was included because it required no increase in the number of moldings and the design was expanded to a 2_V^{7-1} fractional factorial. The ratio of monomers in oligomer productions was placed in the constant category because no large scale effects had been seen. The extraction of unreacted monomers was placed in the constant category for the same reasons. Once the decision was made to select the bleeder cloth technique as a constant, it became desirable to standardize on preforming so that even thickness laminates could be produced. The decision to use vacuum bag conditions at 350°F was made because these conditions result in the maximum volatile loss prior to molding, thus reducing the problem during the molding cycle itself. The preforming pressure was selected at the lowest possible level consistent with the preform having mechanical integrity. The temperature of the mold and press when the preform is introduced was picked at 500°F because higher temperatures appear to magnify the volatile problem and there is no evidence that a lower temperature improves the situation for preformed materials. The initial pressure conditions was picked as the lowest stable reading on the press pressure gage so that there would be the minimum restriction on volatile movement and egress during the initial heating period. We had seen no evidence of the effect of molding time above 30 minutes so that our usual time of 60 minutes was chosen.

TABLE XX

FACTORS IN EXPERIMENTAL DESIGN OF FRACTIONAL FACTORIAL TYPE 2_V^{7-1}

Factors to be Varied	Factor Designation	Levels −	Levels +
Temperature of Oligomer Mixing	X_1	$110^\circ C$	$170^\circ C$
Ratio Monomers (overall) Anhydride to Amine	X_2	1:1	1.04:1
pH of Washed Molding Powder	X_3	1.5	4.5
Temperature at Pressure Application	X_4	$550^\circ F$	$700^\circ F$
Molding Pressure	X_5	1,000 psi	5,000 psi
Molding Temperature	X_6 $(X_1X_2X_3X_4X_5)$	$700^\circ F$	$800^\circ F$
Post Cure	X_7	no	yes

Factors to be Held Constant	Level
Ratio of Monomers in Oligomer Production	2:1 mole ratio
Extraction of Unreacted Monomers	none
Use of Preform	yes
with vacuum bag	yes
temperature of preforming	$350^\circ F$
pressure of preforming	20,000 psi
Use of Bleeder Cloth Molding (2 layers on top and 2 layers on bottom)	yes
Initial Temperature in Molding Cycle	$500^\circ F$
Pressure Prior to Molding Pressure (contact)	50 psi
Time at Molding Temperature	60 minutes

TABLE XXI

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RESPONSE VARIABLES TO BE USED IN FINAL EXPERIMENTAL DESIGN

Responses to be Included in Experimental Design

Flexural properties (ultimate strength, modulus and maximum
deflection)

at 500^OF and 900^OF

Specific Gravity

Hardness

Weight loss after 168 hours aging at 600^OF in air

Other Responses to be Gathered

Weight loss on curing

Platen movement as a function of temperature and time

The levels of the variables were chosen as those most likely to give maximum information from the analysis. The oligomer mixing temperature should change in character above 160°C since any chain extension occurring should go over to the imide-amine form and this should reduce volatiles in the final molding powder. The overall ratio of monomers should be kept reasonably close to 1:1 for maximum cured molecular weight. Considerable evidence indicates that the pH levels chosen should give the most information. The effect of temperature at which the final molding pressure is applied would appear to be a nonsmooth function based on platen movement data. The change from expansion to contraction was quite abrupt so the two temperatures were picked to be above and below the temperature at which this phenomenon is seen. The molding pressure was picked to cover the range used most frequently in compression molding since we have gotten good results in this region. The molding temperature levels were chosen on the basis that temperatures below 700°F have generally resulted in pieces that appeared to lack adequate flow. The upper temperature level may not be high enough to reach the optimum temperature, but press operation limitations dictated the 800°F level. The post cure is a step program holding for 4 hours at multiple intermediate temperatures ending at 800°F and conducted in inert atmosphere (argon).

The matrix for the molding fabrication was set up by listing the independent variables in a horizontal row as column headings and the run numbers 1 through 64 in the left column as the row headings. Each of the variables 1-5 and 7 are then indicated to be molded at the lower level by - sign and at the higher level by a + sign. For the first variable the signs are altered, for the second variable the signs change every second run, for the third variable they change every fourth run, with each succeeding variable changing signs at twice the interval of the preceding one as shown in Table XXII. Since this is not a full factorial design one or more of the variables (in this case one since it is a half replica) is defined by multiplying algebraically the signs for its alias designation. In this design factor six was deliverately confounded with the quintuple interaction $X_1X_2X_3X_4X_5$ which is therefore its alias. Picking this multiple factor interaction insures that factor six will not be confounded by even three factor interactions much less main effects or two factor interactions. The matrix of Table XXII can be expanded in the same fashion (algebraic multiplication of signs) to define the signs for the two factor interactions. This addition to the matrix is used for analysis of these interactions when the response values are determined from the sample testing. If the samples are made in the order the matrix defines, a bias could result if the resin ages for example. Thus the order of sample molding was randomized by associating the runs with a set of numbers from a random number table.

The completed matrix including all response data obtained is given in Table XXIII. The variables listed below were analyzed by the ANOVA method described in reference 15 for main factor correlations and all two factor interactions. These response variables were:

1. Specific gravity
2. Weight loss on Aging 168 hours at 600°F in air
3. Flexural strength at 500°F

TABLE XXII

MATRIX FOR MOLDING PROCESS EXPERIMENTAL DESIGN

Run #		X_1 Oligomer Mix Temp.	X_2 Monomer Ratio Overall Anhdride to Amine	X_3 pH of Washed Molding Powder	X_4 Temperature at Pressure Application	X_5 Molding Pressure	X_6 Molding Temp.	X_7 Post Cure
	− Level	110°C	1:1	1.5-2.0	550°F	1000 psi	700°F	Yes
	+ Level	170°C	1.04:1	4.5-5.0	700°F	5000 psi	800°F	No
1		−	−	−	−	−	−	−
2		+	−	−	−	−	+	−
3		−	+	−	−	−	+	−
4		+	+	−	−	−	+	−
5		−	−	+	−	−	+	−
6		+	−	+	−	−	−	−
7		−	+	+	−	−	−	−
8		+	+	+	−	−	+	−
9		−	−	−	+	−	+	−
10		+	−	−	+	−	−	−
11		−	+	−	+	−	−	−
12		+	+	−	+	−	−	−
13		−	−	+	+	−	−	−
14		+	−	+	+	−	+	−
15		−	+	+	+	−	+	−
16		+	+	+	+	−	−	−
17		−	−	−	−	+	+	−
18		+	−	−	−	+	+	−
19		−	+	−	−	+	−	−
20		+	+	−	−	+	+	−
21		−	−	+	−	+	−	−
22		+	−	+	−	+	+	−
23		−	+	+	−	+	+	−
24		+	+	+	−	+	−	−
25		−	−	−	+	+	−	−
26		+	−	−	+	+	+	−
27		−	+	−	+	+	+	−
28		+	+	−	+	+	−	−
29		−	−	+	+	+	+	−
30		+	−	+	+	+	−	−
31		−	+	+	+	+	−	−
32		+	+	+	+	+	+	−
33		−	−	−	−	−	+	+
34		+	−	−	−	−	+	+
35		−	+	−	−	−	+	+
36		+	+	−	−	−	+	+
37		−	−	+	−	−	+	+
38		+	−	+	−	−	−	+
39		−	+	+	−	−	+	+
40		+	+	+	−	−	+	+
41		−	−	−	+	−	+	+
42		+	−	−	+	−	−	+
43		−	+	−	+	−	−	+
44		+	+	−	+	−	+	+
45		−	−	+	+	−	+	+
46		+	−	+	+	−	+	+
47		−	+	+	+	−	+	+
48		+	+	+	+	−	+	+
49		−	−	−	−	+	+	+
50		+	−	−	−	+	−	+
51		−	+	−	−	+	−	+
52		+	+	−	−	+	+	+
53		−	−	+	−	+	+	+
54		+	−	+	−	+	+	+
55		−	+	+	−	+	+	+
56		+	+	+	−	+	−	+
57		−	−	−	+	+	+	+
58		+	−	−	+	+	+	+
59		−	+	−	+	+	+	+
60		+	+	−	+	+	+	+
61		−	−	+	+	+	+	+
62		+	−	+	+	+	−	+
63		−	+	+	+	+	−	+
64		+	+	+	+	+	+	+

TABLE XXIII

Complete Molding Process Experimental Design Matrix

Matrix Number	Resin Number	Molding Number	Oligomer Mixing Temp.°C	Overall Monomer Ratio	pH of Washed Molding Powder	Temperature @ Application °F	Molding Pressure psi	Molding Temperature °F	Post Cure yes or no	Wt. Loss in Molding	Specific Gravity gm/cc	Barcol Hardness	Wt. Loss on 168 Hrs. Aging in air @ 600°F %	Flexural Strength @ 500°F psi	Flexural Modulus @ 500°F (psi x 15⁰)	Flexural Strength @ 900°F psi	Flexural Modulus @ 900°F (psi x 15⁰)
XD-1	478-142-11A	1022-134	110	1:1	1.5	550	1000	700	no	12.9	1.340	77	71.	8650	0.57	3540	0.27
XD-2	478-142-170A	1022-10	170	1:1	1.5	550	1000	800	no	22.8	1.100	70	23.	7030	0.38	1580	0.049
XD-3	478-138-110A	1022-152	110	1.04:1	1.5	550	1000	800	no	24.4	0.930	47	11.8	739	0.52	722	0.21
XD-4	478-138-170A	1028-26	170	1.04:1	1.5	550	1000	700	no	9.5	0.822	40	29.7	5900	0.31	1410	0.11
XD-5	478-142-110B	1022-110	110	1:1	4.5	550	1000	800	no	17.2	1.310	63	23	2810	0.57	983	0.13
XD-6	478-142-170B	1028-32	170	1:1	4.5	550	1000	700	no	13.5	1.264	74	6.6	2550	0.52	1010	0.10
XD-7	478-138-110B	1028-20	110	1.04:1	4.5	550	1000	700	no	12.5	1.097	73	8.01	3600	0.43	1630	0.052
XD-8	478-138-170B	1028-40	170	1.04:1	4.5	550	1000	800	no	21.8	1.178	70	5.7	5160	0.86	1740	0.17
XD-9	478-142-170A	1022-144	110	1:1	1.5	750	1000	800	no	23.6	1.254	69	58.	4290	0.47	1030	0.28
XD-10	478-142-170A	1022-120	170	1:1	1.5	700	1000	700	no	15.9	1.160	68	11.5	5860	0.48	2130	0.28
XD-11	478-138-110A	1022-146	110	1.04:1	1.5	700	1000	700	no	14.4	1.230	71	4.77	11600	0.55	631	0.057
XD-12	478-138-170A	1028-28	170	1.04:1	1.5	750	1000	800	no	25.0	0.739	73	50.0	1000	0.30	756	0.023
XD-13	478-142-110B	1028-12	110	1:1	4.5	700	1000	700	no	14.7	1.238	71	16.	12100	0.60	1280	0.029
XD-14	478-142-170B	1022-138	170	1:1	4.5	750	1000	800	no	19.0	1.233	62	4.96	7095	0.52	329	0.048
XD-15	478-138-110B	1022-16	110	1.04:1	4.5	750	1000	800	no	21.9	1.153	65	6.56	7080	0.59	1600	0.13
XD-16	478-138-170B	1028-38	170	1.04:1	4.5	700	1000	700	no	16.4	1.297	71	1.66	9250	0.62	459	0.031
XD-17	478-142-110A	1022-136	110	1:1	1.5	550	5000	800	no	21.6	1.247	66	47.	1450	0.23	488	0.085
XD-18	478-142-170A	1022-126	170	1:1	1.5	550	5000	700	no	10.1	1.130	60	47.5	7130	0.40	1960	0.15
XD-19	478-138-110A	1022-150	110	1.04:1	1.5	550	5000	700	no	12.9	1.199	65	10.3	10500	0.42	1500	0.30
XD-20	478-138-170A	1028-24	170	1.04:1	1.5	550	5000	800	no	25.0	0.800	73	50.0	1000	0.30	700	0.030
XD-21	478-142-110B	1022-128	110	1:1	4.5	550	5000	700	no	11.2	1.344	66	8.0	10300	0.70	1540	0.33
XD-22	478-142-170B	1028-32	170	1:1	4.5	550	5000	800	no	18.2	1.295	73	7.29	6160	0.65	2020	0.75
XD-23	478-138-110B	1028-4	110	1.04:1	4.5	550	5000	800	no	18.3	1.190	72	6.46	3760	0.53	1750	0.18
XD-24	478-138-170B	1028-42	170	1.04:1	4.5	550	5000	700	no	15.0	1.268	68	2.61	9620	0.79	276	0.034
XD-25	478-142-110A	1022-108	110	1:1	1.5	700	5000	700	no	17.3	1.363	66	10.4	3190	0.52	3510	0.38
XD-26	478-142-170A	1028-30	170	1:1	1.5	750	5000	800	no	23.5	1.244	70	14.8	3960	0.64	1310	0.31
XD-27	478-138-110A	1028-2	110	1.04:1	1.5	750	5000	800	no	22.5	1.241	72	5.20	5100	0.64	1280	0.34
XD-28	478-138-170A	1028-22	170	1.04:1	1.5	750	5000	800	no	8.9	1.167	69	26.	4220	0.73	3750	0.23
XD-29	478-142-110B	1022-132	110	1:1	4.5	750	5000	800	no	24.9	1.253	69	25.	896	0.59	2110	0.25
XD-30	478-142-170B	1022-140	170	1:1	4.5	700	5000	700	no	15.6	1.311	58	3.96	1830	0.42	345	0.047
XD-31	478-138-110B	1028-18	110	1.04:1	4.5	700	5000	700	no	16.3	1.314	73	2.72	5100	0.64	216	0.01
XD-32	478-138-170B	1028-36	170	1.04:1	4.5	750	5000	800	no	18.9	1.278	69	1.80	12500	0.72	1030	0.056
XD-1 2nd	478-142-110A	1028-48	110	1:1	1.5	550	1000	700	no	17.9	1.267	75	20.	9340	0.52	2610	0.22
XD-5 2nd	478-142-110B	1028-6	110	1:1	4.5	550	1000	800	no	15.2	1.303			8290	0.50	4770	0.28
XD-17 2nd	478-142-110A	1028-44	110	1:1	1.5	550	5000	800	no	27.0	1.186	73	50.	1210	0.37	1190	0.23
XD-25 2nd	478-142-110A	1028-8	110	1:1	1.5	700	5000	700	no	14.7	1.363	72		3190	0.52	3510	0.38
XD-12 2nd	478-138-170A	1028-52	170	1.04:1	1.5	750	1000	800	no	26.2	0.739	73	35.			756	0.023
XD-1 PC	478-142-170A	1022-134	110	1:1	1.5	550	1000	700	yes		1.236	75	6.06	12700	0.511	2030	0.20
XD-2 PC	478-142-170A	1028-10	170	1:1	1.5	550	1000	800	yes		1.076	75	19.	6300	0.36	2870	0.096
XD-3 PC	478-138-110A	1022-152	110	1.04:1	1.5	550	1000	800	yes		0.898		33	1310	0.20	1020	0.045
XD-4 PC	478-138-170A	1028-26	170	1.04:1	1.5	550	1000	700	yes		0.556		60.0	3000	0.30	1200	0.10
XD-5 PC	478-142-110B	1022-110	110	1:1	4.5	550	1000	800	yes		1.266	74	4.0	6080	0.58	3140	0.27
XD-6 PC	478-142-170B	1028-34	170	1:1	4.5	550	1000	700	yes		1.243		11.8	2210	0.31	1550	0.11
XD-7 PC	478-138-110B	1028-20	110	1.04:1	4.5	550	1000	700	yes		1.131	64.5	42.	5290	0.37	2730	0.27
XD-8 PC	478-138-170B	1028-40	170	1.04:1	4.5	550	1000	800	yes		1.124		8.1	6430	0.73	3440	0.15
XD-9 PC	478-142-110A	1022-144	110	1:1	1.5	750	1000	800	yes		1.116		46.7	2410	0.42	2410	0.42
XD-10 PC	478-142-170A	1022-120	170	1:1	1.5	700	1000	700	yes		0.796	51	40.	2630	0.53	1300	0.20
XD-11 PC	478-138-110A	1022-146	110	1.04:1	1.5	700	1000	700	yes		1.053	74	49.4	5980	0.54	1670	0.31
XD-12 PC	478-138-170A	1028-28	170	1.04:1	1.5	750	1000	800	yes		0.689		44.	3180	0.18	1500	0.10
XD-13 PC	478-142-110B	1028-12	110	1:1	4.5	700	1000	700	yes		1.212	57	41.	3940	0.26	1950	0.17
XD-14 PC	478-142-170B	1022-138	170	1:1	4.5	750	1000	800	yes		1.245	71	5.6	2910	0.51	1650	0.22
XD-15 PC	478-138-110B	1028-16	110	1.04:1	4.5	750	1000	800	yes		1.157	76	9.9	5120	0.64	2510	0.25
XD-16 PC	478-138-170B	1028-38	170	1.04:1	4.5	700	1000	700	yes		1.175		3.6	4510	0.65	2810	0.10
XD-17 PC	478-142-110A	1022-136	110	1:1	1.5	550	5000	800	yes		1.091		35.	1170	0.26	729	0.11
XD-18 PC	478-142-170A	1022-126	170	1:1	1.5	550	5000	700	yes		0.855		15.	6320	0.30	1900	0.10
XD-19 PC	478-138-110A	1022-150	110	1.04:1	1.5	550	5000	700	yes		0.876		9.5	1170	0.39	371	0.016
XD-20 PC	478-138-170A	1028-24	170	1.04:1	1.5	550	5000	800	yes		0.600		80.0	1000	0.25	600	0.050
XD-21 PC	478-142-110B	1022-128	110	1:1	4.5	550	5000	700	yes		1.250		5.2	9430	0.59	1500	0.30
XD-22 PC	478-142-170B	1028-32	170	1:1	4.5	550	5000	800	yes		1.228		7.2	3100	0.62	1730	0.097
XD-23 PC	478-138-110B	1028-4	110	1.04:1	4.5	550	5000	800	yes		1.203		5.8	3090.	0.62	1820	0.17
XD-24 PC	478-138-170B	1028-42	170	1.04:1	4.5	550	5000	700	yes		1.128		3.2	3610	0.58	1890	0.040
XD-25 PC	478-142-110A	1022-108	110	1:1	1.5	700	5000	700	yes		1.213		26.0	1920	0.45	1740	0.30
XD-26 PC	478-142-170A	1028-30	170	1:1	1.5	750	5000	800	yes		1.209		9.8	2940	0.63	1440	0.29
XD-27 PC	478-138-110A	1028-2	110	1.04:1	1.5	750	5000	800	yes		1.237		13.9	3290	0.54	1100	0.25
XD-28 PC	478-138-170A	1028-22	170	1.04:1	1.5	700	5000	700	yes		0.766		75.0	3000	0.10	2000	0.10
XD-29 PC	478-142-110B	1022-132	110	1:1	4.5	700	5000	800	yes		1.192		30.7	1300	0.54	561	0.004
XD-30 PC	478-142-170B	1022-140	170	1:1	4.5	700	5000	700	yes		1.193		8.6	7180	0.55	2020	0.034
XD-31 PC	478-138-110B	1028-18	110	1.04:1	4.5	700	5000	700	yes		1.192		5.4	3870	0.59	1830	0.048
XD-32 PC	478-138-170B	1028-32	170	1.04:1	4.5	750	5000	800	yes		1.245		6.4	7500	0.66	3860	0.14
XD-1 2nd PC	478-142-110A	1028-48	110	1:1	1.5	550	1000	700	yes		1.135	73	9.6			1270	0.16
XD-5 2nd PC	478-142-110B	1028-6	110	1:1	4.5	550	1000	800	yes	All without post cure							
XD-17 " "	478-142-110A	1028-44	110	1:1	1.5	550	5000	800	yes		1.097		37.	5160	0.45		
XD-25 " "	478-142-110A	1028-8	110	1:1	1.5	700	5000	700	yes		1.203		59.	3650			

57

Exploded on molding; estimated values
warped and split during post cure; estimated values

4. Flexural Modulus at 500°F
5. Flexural Strength at 900°F
6. Flexural Modulus at 900°F

In the analysis by the ANOVA method, all higher factor interactions were assumed negligible and combined into the error estimate. Based on this analysis, the specific gravity correlated with all independent variables except the molding temperature at/or higher than the 99 percent confidence level and with eight two factor interactions at/or higher than the 95 percent level. As an indication of the overall correlation the error sum of squares for the specific gravity was less than 10 percent of the total sum of squares. For all other response variables this ranges from 34 percent to 45 percent. The other response variables correlate at most with two main factors and five two factor interactions. Table XXIV lists the F ratio values for all the main factors and two factor interactions that are signnificant at or above the 95 percent confidence level. Improved flexural modulus at 900°F and specific gravity require lower oligomer mixing temperature. The BSA solutions have a minimum mixing temperature of $\sim$ 50°C below which crystallization can occur. Less chain extension would be expected during the mixing at the lower temperatures. This may allow better flow which in turn gives better densification. Higher density would in turn give better oxidation resistance and better material utilization, both acting to give an increase in 900°F modulus. The lower monomer ratio is the 1:1 stoichiometry which is the ideal for highest molecular weight. Both responses should increase as the molecular weight increases. It is somewhat surprising that 500°F modulus and the strengths do not also show a correlation. This lack of correlation is not understood. The highest pH for the molding powder appears best since the specific gravity and 500°F modulus both increase and the weight loss on aging decreases. Both the temperature at pressure application and the molding pressure correlate positively with the specific gravity though not as strongly as do X_1, X_2, X_3, and X_7. The molding temperature appears to correlate only with the 500°F flexural strength. This negative correlation which is good but not the best would mean that the lower molding temperatures gave on the average the higher flexural strengths at 500°F. In light of this correlation it is again surprising that there is no correlation with 900°F strength. The fact that one test temperature is below and the other test temperature above the molding temperature may account for this phenomenon but certainly any causal relationships are not simple. Finally, the postcuring lowers the specific gravity and the 500°F flex strength while the 900°F flex strength increases. The removal of unstable (at 800-900°F) molecular fragments during the post curing might well be the mechanism by which the strength improvement derives. The fragments could well be stable at 500°F and thus contribute to the 500°F strength as well as the specific gravity.

Typical temperature-platen movement data for these runs are given in Figure 17. These data were obtained by placing a linear variable differential transformer (LVDT) to read the relative platen movements of the press during

58

TABLE XXIV

MATRIX OF SIGNIFICANT CORRELATIONS FROM MOLDING PROCESS EXPERIMENTAL DESIGN

Factor(s)	Specific Gravity	Wt. Loss on Aging	500°F Flexural Strength	500°F Flexural Modulus	900°F Flexural Strength	900°F Flexural Modulus
X1 Oligomer Mix Temp.	38.96***					4.20*
X2 Monomer Ratio	63.73***					5.62*
X3 Molding Powder pH	108.5***	31.28***		1843***		
X4 Temp. @ Press. Appl.	11.02**					
X5 Molding Pressure	10.05**					
X6 Molding Temp.			7.80**			
X7 Post Cure	38.22***		4.53*		6.72*	
X1X2		12.88**				
X1X3	48.3***	6.09*		6.70*		
X1X4						
X1X5						
X1X6			7.03*	3.14*		
X1X7						
X2X3	22.0***			8.78**	8.08**	
X2X4	12.0**		6.60*			
X2X5	4.11*					
X2X6						
X2X7		5.13*				
X3X4	7.46*			3.31*		13.20**
X3X5						
X3X6					11.08**	
X3X7	10.7**				12.00**	
X4X5	6.96*				6.36*	
X4X6						
X4X7						
X5X6						
X5X7					4.46*	7.25*
X6X7	9.57**					

Note: Single asterisk denotes correlation at the 95% confidence level

Double asterisk denotes correlation at the 99% confidence level

Triple asterisk denotes correlation at the 99.9% confidence level
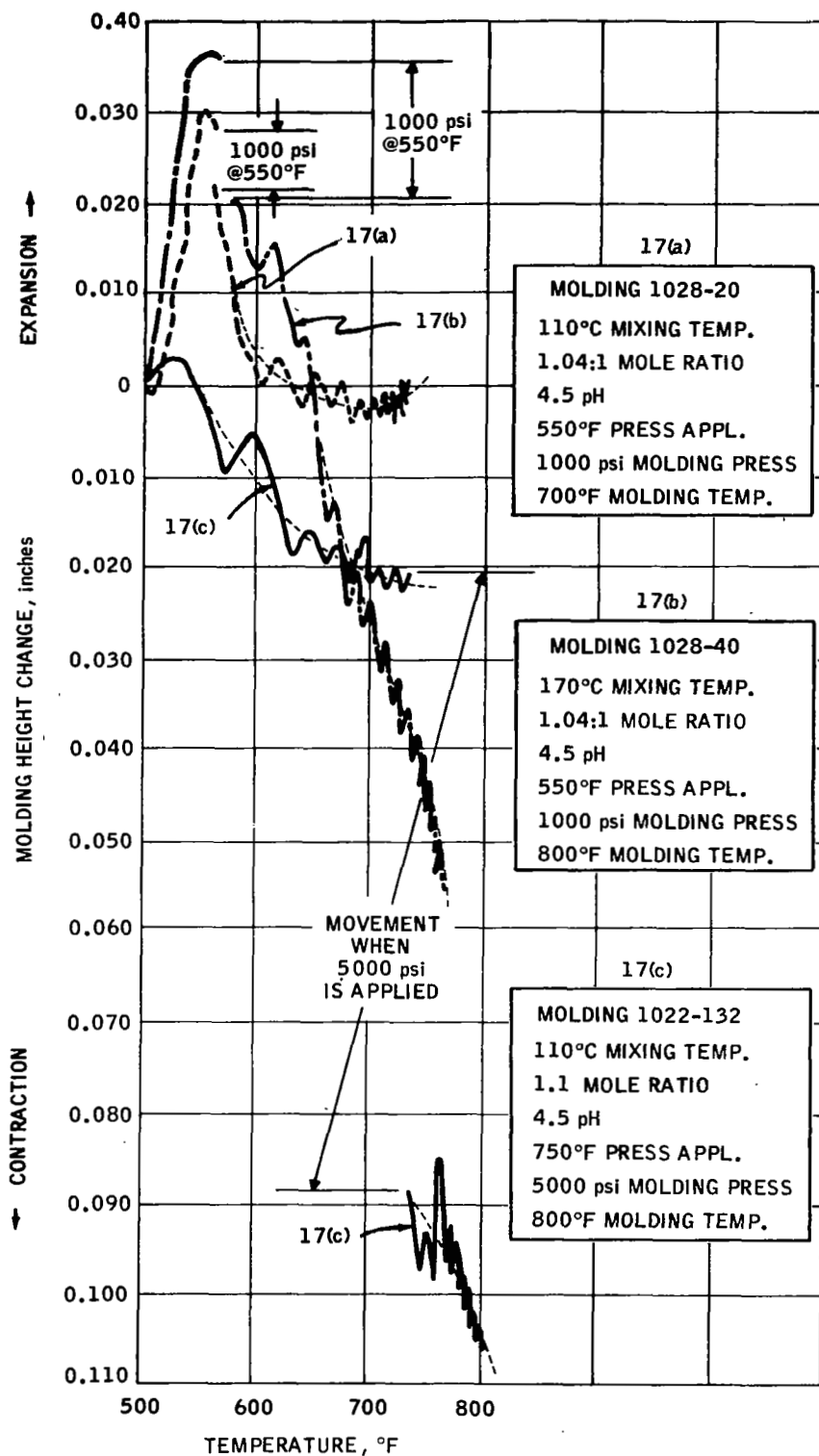
Figure 17 CHANGE IN MOLDING POWDER THICKNESS AS A FUNCTION OF
TEMPERATURE DURING MOLDING

70-0212

60

the actual molding cycle. The output of this LVDT was fed to the X input of an X-Y recorder while the Y input was fed from a thermocouple taped to the mold surface. The resulting plot shows the expansion and contraction of the mold and resin as a function of temperature during the molding cycle. Note particularly that there is a rather abrupt change from expansion to contraction between 500 and 550°F. This abrupt change may well indicate the onset of flow in the polymer system.

Several equipment modifications were necessary in the sensing and recording equipment before the noise level was reduced to the point shown on Figure 17. The high frequency variations thought at first to be associated with resin breathing in the curves were found to be a function of the on-off control of the platen heaters. Thus the average of the alternations, shown by a dotted line, is the true movement of the resin.

The molding behavior of the resins can generally be divided into those that show continual contraction throughout the "cure" portion of the molding cycle (Figures 17 b and 17 c) and those that show little or no contraction or movement during this portion of the mold cycle (Figure 17 a). One feels that this movement or lack of it must be tied in with some basic structural or chemical differences but there does not appear to be any correlation with the independent variables or their two factor interactions. There is a possibility that higher molding temperature gives more movement during cure since more of the samples that show flow during cure are 800°F cure temperature samples. However further work is necessary to define the utility of this as a tool for improving our knowledge of the molding process.

These relationships were taken into account in deciding the molding cycle and molding powder parameters for the deliverable items. Table XXV is the molding cycle to be used for those moldings.

The preform technique used for the molding process in the experimental design was discarded when the decision was made on the molding cycle for the deliverable items. The decision was based on several factors:

1. The press time required for the preform-press mold cycle was twice as long as the straight press mold cycle.

2. Additional time was required to sand the preform to fit into the mold due to the elasticity of the material and mold.

3. We devised a simple technique for smoothing the molding powder in the mold repetitively so that even thickness parts would result.

4. A simple preforming type of operation in situ gave sufficient compaction to get good heat transfer and effective molding.

61

TABLE XXV

DELIVERABLE ITEM MOLDING CYCLE

1. Preheat press to 500°F

2. Place 2 layers breather cloth in mold

3. Pour in molding powder - smooth to even thickness.

4. Add two layers of breather cloth on resin and close mold.

5. Place mold in press and close press to contact pressure (50-100 psi).

6. Raise set point to 800°F.

7. When mold reaches 700°F apply 5000 psi pressure.

8. Hold at 800°F for 1 hour. Maintain 5000 psi pressure.

9. Cool under pressure to 400°F.

10. Remove from mold.

V. SCALE-UP

Although the oligomer process is inherently very flexible because many parameters may be varied to produce the specific molecule required, certain aspects must be controlled very precisely to prevent large scale branching or cross-linking. Two of the critical process areas are longer heat-up time associated with larger batches and the local stoichiometry during oligomer synthesis and mixing.

The heatup time was decreased from 3 hours to 1 hour to 45 minutes and finally to 24 minutes over a nine-run sequence. This appears to be the minimum time possible without overheating the reaction vessel walls and causing monomer degradation or premature solvent degradation. The amount of benzene removed during these steps dropped from a ratio of one milliliter of benzene for every two milliliters of water to 1 ml of benzene to every 11 to 12 ml of water. This corresponds to a mole ratio change from 1:10 to 1:50 or from 10 percent hydrolysis to about 2 percent hydrolysis and appears to be acceptable.

Further reductions in heating time could be realized by using flow type heaters with very high surface to volume ratios in contrast to the cylindrical resin kettles used for the synthesis during this contract.

Initial scale-up from the 1/2 lb. per batch level was attempted in stainless steel equipment. This run was a complete failure due to degradation of both the anhydride-BSA solution and the amine-BSA solution prior to mixing. Whether the degradation was due primarily to the metal walls of the vessels or the interaction between the less pure BSA purchased in bulk and the walls was not obvious. However, pure BSA and glass equipment was used for all subsequent syntheses.

The increased mixing problems were first observed in the oligomer synthesis when scaling up from the 100 gram level to the one pound (453.6 grams) level. A local excess of one monomer is desired to react with the second monomer to prevent formation of unwanted high molecular weight species. In scaling up, faster addition rates were required to keep total addition time at the same value as the smaller early runs. The increase in addition rates was larger than the increase in stirring rates and small mounds of gel formed at the addition point. This was probably due to a shift in the local stoichiometry away from the 2:1 ratio toward the 1:1 ratio which gives maximum molecular weight. Increased mixing and splitting of the single addition stream into two or more streams reduced the gel formation significantly. The tendency toward branching was reduced by making the more stable amine capped oligomer one day, the anhydride capped oligomer the following day, and mixing them together as soon as the latter solution cooled to the required temperature.

The intensity of mixing actually applied probably decreased some
since the volume increased by a factor of ten from the early 250 gram
level to the 5 lb. (2258 gms.) and the horsepower of the stirrer did
not increase commensurately. As a result it is anticipated that the
actual mixing conditions were further from the ideal for the large batches
than for the small. The physical problems of stirring 50 gal. of water
violently reduced the precipitation officiency and the first attempts
to precipitate rapidly resulted in a tar like layer on the bottom of the
precipitation tank which had to be broken up in a blender so that washing
could be completed. However, the washing was much easier once the
precipitate was broken up because the solids would drop to the bottom
rapidly and never went through the stage of colloidal suspension properties.
Most of the large batches ($> 2\#$) were molecularly mixed at 60°C which
could account for the ease of precipitation and washing.

One of the more subtle problems to answer in scale-up is whether
quality of the resulting product is the same as, or better or worse
than before. In this case quality can only be judged by comparison
of physical or mechanical properties of moldings (such as specific gravity
and flexural properties) since no a priori standard was available.
Reproducibility was even harder to define until multipound batch levels
were reached because the wide range of variables to be investigated seldom
left any resin available for duplication. The most dramatic indication
of homogeneity within a resin batch and reproducibility of molding
conditions was shown when the deliverable rods were fabricated.

The recommended molding cycle that evolved from the experimental design
worked very well in producing eleven 5 in. x 1 in. bars of very close
physical properties for machining into the deliverable rods 5 in. long.
by 1/4 in. diameter. The machining conditions for making the rods are
given in Appendix A. The average specific gravity of the 30 rods was
1.347; maximum and minimum values were 1.36 and 1.33, a variation of only
0.03 specific gravity units. The average weight loss from the molding
process (14.6%) appeared to correlate with chronological time, there
being an 11.2 percent loss for the first bar, and a 15.8 percent for
the last one. Such a correlation might imply that atmosphereic con-
ditions such as ambient relative humidity could have an effect. Evidence
of the similarity amongst these moldings is shown in the IR spectra from
four of the bars (Figure 18). A comparison of Figure 18 b (molding
1028-73 which had the clearest spectra) with the band list given in
reference 16 shows that only two of the 13 bands listed for the pyrrones
are missing. The four spectra are very similar with the same prominent
bands shown in each spectra and very close relative heights for these
bands. For example, the peaks at 1750 cm^{-1}, 1610 cm^{-1}, and 1240 cm^{-1}
are all about the same in each spectra and the peaks at 800 cm^{-1} are
also similar to each other in height and less than the first three.

One of the two missing bands (that at 1470 cm^{-1}) shows some unlikely
appearances and disappearances if this is truly a pyrrone band. Generally
a band in the 1450-1500 cm^{-1} region is present in anhydride capped oligomers
no matter what solvent was used for synthesis but does not appear in the
spectra for amine capped oligomers. It also shows up in some mixed oligomers
but not in others. None of the oligomer route moldings showed a band in this

64

18(a)

18(b)

18(c)

18(d)

2000   1700   1400   1100   800

70-0213   FREQUENCY (CM^{-1})
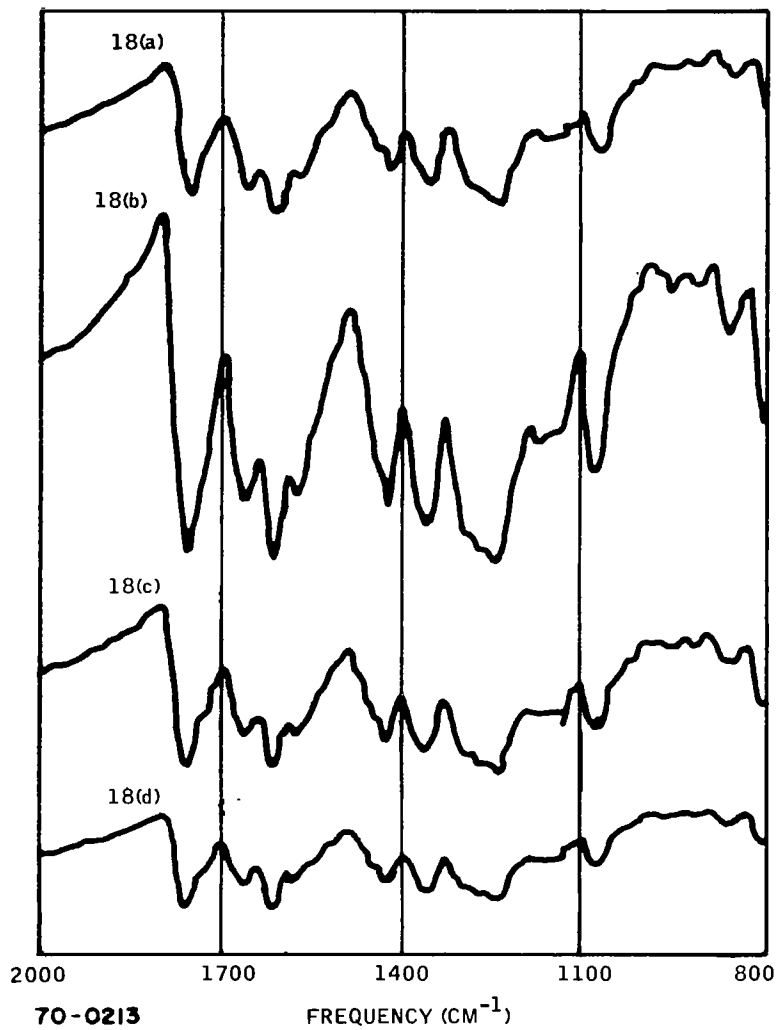
Figure 18 COMPARISON OF IR SPECTRA OF FOUR OLIGOMER ROUTE PYRRONE MOLDINGS AS AN INDICATION OF THE REPRODUCIBILITY OF THE MOLDING PROCESS

65

region, including the the 5 x 1 in. bars (Figure 18), the first molding made, the highest density molding made (synthesized in DMF and mixed in BSA), a molding made from oligomers that were extracted and then mixed and a molding used for a deliverable item. None of the peaks seen in any of the other spectra have both the intensity and frequency shown by this peak in some of the spectra in the cited work. It must be pointed out that the spectra in reference 16 for Me_2-DAB salt as a function of cure show no such peak in the most cured state and only a weak peak at intermediate cures. In fact it may be that the strong peak at 1500 cm^{-1} slowly broadens and shifts to lower wave numbers (lower frequency) before fading out. This could be tied in with increasing rigidity in the backbone as cyclization proceeds.

Larger moldings (8-1/2 x 3-1/4 x 1/4 in.) for the deliverable bars were attempted next and the molding data for the first four moldings are given in Table XXVI. These moldings showed substantial cracking. The cracks in molding 1028-79 were in the thickness direction but those in the other three moldings were generally in the length-width plane. The cracks in the thickness direction appeared to be shrinkage cracks so that modifications to the molding cycle were made to reduce the effect of such forces.

These modifications were longer times at the mold temperature to drive out volatiles while under pressure and to give a more complete cure, and early release of the pressure to allow the molding to move independently of the mold during the cooling period. These changes apparently prevented the shrinkage cracks from occurring but also apparently caused enough buildup in internal pressure from trapped volatiles to cause the second kind of crack. For the most part these cracks did not show at any of the surfaces but were detected by through transmission of ultra sound (1-5 MHz) using standard nondestructive testing (NDT) techniques.

Since the resin batch was not held constant over the four moldings, resin variation was considered to be a reason for the cracking. In order to test this possibility, four 5 x 1 in. moldings were made, 2 each from 1039-1 and 1039-5 resins. One of each was molded by the cycle used when molding for rod production and the other two were molded with the longer molding time and early pressure release used for the last three 8-1/2 x 3-1/4 in. moldings. The results are shown in Table XXVII. Evidently the resin batches are both satisfactory. The three major changes are the longer time at the molding temperature, the early pressure release and the higher pressure. Certainly one would anticipate that higher pressure (2.7X) could suppress such cracks. However the experience in molding the 5 x 1 in. bars for rod production where pressure ranged from 6,700 psi to 13,700 psi without cracks of either type suggest that there is no major effect of pressure. If this be true then longer time at molding temperature and early pressure release are the main cause of the cracking.

TABLE XXVI

MOLDING CONDITIONS FOR INITIAL $8\frac{1}{2}$" x $3\frac{1}{4}$" PLATES

Molding Number	Resin	Temp. of Pre-heated Mold	Temp. of Press. Appl.	Mold Press.	Molding Temp.	Molding Time	Holding Temp.	Holding Time	Temp. at Press. Release	Specific Gravity
1028-79	1039-1	500°F	700°F	5000 psi	800°F	60 min.	none	-	Room Temperature	1.28
1028-82	1039-4	500°F	700°F	5000 psi	800°F	120 min.	none	-	750°F	1.27
1028-84	1039-5	600°F	700°F	5000 psi	800°F	180 min.	700°F	120 min.	700°F	1.29
1028-86	1039-5	500°F hold at 500°F for 1 hour	700°F	5000 psi	800°F	180 min.	700°F	120 min.	700°F	1.26

TABLE XXVII

EFFECT OF MOLDING TIME AND PRESSURE RELEASE ON MOLDING SPECIFIC GRAVITY AND CONTIGUITY

Molding	Resin Number	Press. Temp.	Temp. @ Press. App.	Molding Pressure	Molding Temp.	Time at Mold Temp.	Hold Temp.	Hold Time	Temp. at Press. Release	Specific Gravity	Cracks
1028-78	1039-1	500°F	700°F	13,700 psi	800°F	60 min.	none	–	500°F	1.32	no
1028-85	1039-5	500°F	700°F	5,000 psi	800°F	180 min.	700	120 min.	700°F	1.28	yes
1028-87	1039-1	500°F	700°F	5,000 psi	800°F	120 min.	none	–	750°F	1.25	yes
1028-88	1039-5	500°F	700°F	13,700 psi	800°F	60 min.	none	–	500°F	1.33	no

The longer time at temperature should in fact cause more volatile generation within the molding since more complete cyclization should result from this change in molding cycle. These volatiles could be more completely trapped than those generated earlier in the cycle because the resin at the mold surfaces would cure first and creat a much greater diffusion barrier to volatile egress. Early pressure release at temperatures of 750°F or 700°F where resin strengths are not as high and internal gas pressure very high would be the right combination of conditions for cracks to be generated. Further moldings to test this hypothesis were made next.

Molding 1028-91 was limited to 60 minutes at temperatures above 775°F instead of the 60 minutes or more at 800°F molding cycle used in previous 9-1/2 x 3-1/4 in. moldings. As shown in Table XXVIII the specific gravity was slightly low (1.30) but there were not cracks according to NDT evaluation. Molding 1028-93, a repeat with the same resin powder and conditions, had significant cracks so the time at temperatures above 775°F was reduced to 50 minutes. Molding 1028-95 had a better specific gravity, 1.31, and no cracks. The problem, however, was not solved yet as the next molding (1028-99), made from a different resin batch, was molded with only 45 min. at 775°F + and had several cracks parallel to the large surface. A reduction in temperature to 750°F coupled with a 60 minute residence time gave three good moldings (1028-100-1, -2, -3) with this same batch of resin. Note though that 1028-100-2 was not compressed evenly throughout the whole piece resulting in one end being thin and the powder not well bonded to itself. Whether the mold cocked in seating or the powder was not spread evenly in the mold is not known.

The next two moldings (1028-102-1, -2) were again made from a new batch of resin but keeping the molding procedure the same, namely 60 min. at 750°F, resulted in two crack free pieces of the same specific gravity (1.32). However, the third molding (1028-102-3) from the 1039-15 resin batch, run under apparently identical conditions, had a lower specific gravity (1.30) and large cracks parallel to the surface. The study of the scaled up molding process for 8-1/2 x 3-1/4 in. moldings was hampered by the fact that a full 1-1/2# batch of resin would only give three or four moldings since each required 180 grams of molding powder. Thus many comparisons of effects were complicated by unavoidable changes in resin as well as the deliberate changes in the molding cycle.

Either the molding process was extra sensitive when making large moldings or the batch to batch synthesis variations were more critical than previous experience indicated because the large moldings varied drastically in interior integrity (splitting) according to NDT inspection without apparent changes in molding cycle or synthesis conditions. An extreme example of this is the molding from resin batch 1039-16 (Table XXVIII). Although this resin batch was made ostensibly in identical fashion to 1039-15 and 1039-12 and all four moldings (1028-104-1,-2,-3,-4) made from the resin were done under the same molding conditions (those that gave five good moldings out of six attempted under these conditions), all four from 1039-16 had major splits parallel to the large surface and a maximum specific gravity of 1.26. Also the mechanical properties of material from the good sections

TABLE XXVIII

MOLDING CONDITIONS FOR DELIVERABLE ITEM PLATES

Molding Number	Resin Number	Preform Conditions Press. k psi	Temp. °F	Time Min.	Initial Temp. °F	Press. k psi	Time Min	Final Temp. °F	Press. k psi	Time @ Temp Min.	Wt. Loss %	Specific Gravity	Remarks
1028-90	1039-5				600			775+	5	60	14.7	1.30	8½ x 3¼", few cracks - rest good
1028-91	1039-8				600			775+	5	60	13.7	1.30	8½ x 3¼ delivered
1028-93	1039-8				600			775+	5	60	14.2	1.29	8½ x 3¼", partial cracking parallel to surface
1028-95	1039-8				600			775+	5	50	12.0	1.31	8½" x 3¼" delivered
1028-99	1039-12				600			775+	5	45	13.5	1.30	8½ x 3¼", Partial split parallel to surface
1028-100 1	1039-12				500			750	5	60	13.1	1.30	8½", x 3¼", deliverd
1028-100-2	1039-12				500			750	5	60	12.5	1.31	8½" x 3¼",about 3/4 good, thin other 1/4
1028-100-3	1039-12				500			750	5	60	12.6	1.32	8½" x 3¼", delivered
1028-102-1	1039-15				500			750	5	60	12.8	1.32	8½" x 3¼", delivered
1028-102 2	1039-12				500			750	5	60	12.5	1.31	8½" x 3¼", about 3/4 good, thin other 1/4
1028-100-3	1039-12				500			750	5	60	12.6	1.32	8½" x 3¼", delivered
1028-102-1	1039-15				500			750	5	60	12.8	1.32	8½" x 3¼", deliverd
1028-102-2	1039-15				500			750	5	60	13.6	1.32	8½" x 3¼", delivered
1028-102-3	1039-15				500			750	5	60	13.1	1.30	8½" x 3¼", split
1028-104-1	1039-16				600			750	5	60			8½" x 3¼" on cool down molding split upon release of pressure at 500°F
1028-104-2	1039-16				600			750	5	60	14.2	1.26	8½" x 3¼" partial split parallel to surface
1028-104-3	1039-16				600			750	5	60	14.2	1.24	8½" x 3¼" split parallel to surface
1028 104-4	1039-16				600			750	5	60			8½" x 3¼" on cool down molding split upon release of pressure at 500°F
1028 108	1039-23	10	R.T.	1 max.	500			750	5	60	14.4	1.30	8½" x 3¼" delivered
1028 109	1039-23	10	R.T.	1 max.	500		30	800	5	60			molding shows large cracks through thickness, 8½" x 3¼"
1028-110	1039 23				500			800	5	60			molding shows large cracks through thickness, 8½" x 3¼"
1028 111	1039-23	1	R.T.	1 max.	R.T.	0.2		800	0.2	60	16.6	.948	after preform entire molding was at 200 psi, does not appear cured, 8½" x 3¼"
1028 112 A	1039 23	5	R.T.	1 max.	500			750	5	60	14.8	1.29	good center, poor ends; 8½" x 3¼"
1028-112-B	1039-23	5	R.T.	1 max.	500			750	5	60	13.6	1.30	delivered, 8½" x 3¼"
1028 113-A	1039-23	5	R.T.	1 max.	500			750	5	60	13.2	1.32	delivered 2/3, 8½" x 3¼"
1028-113-B	1039-23	5	R.T.	1 max.	500			750	5	60	13.6	1.30	delivered, 8½" x 3¼"
1028 113-C	1039-23	5	R.T.	1 max.	500			750	5	60	14.0	1.30	delivered, 8½" x 3¼"
1028-114-B	1039-23	5	R.T.	1 max.	500			750	5	60	14.9	1.30	delivered, 8½" x 3¼"
1028 114C	1039-23	5	R.T.	1 max.	500			750	5	60	11.9	1.32	delivered, 8½" x 3¼"

Note: All resin powder was made and mixed in BSA solution. Synthesis temperature was 392°F; molecular mix temperature 140°F and the resin was washed to a pH of 4.5: the temperature at which 5000 psi pressure was applied was 700°F.

of molding 1028-90 which had a moderately good specific gravity and relatively few cracks to avoid, were lower than expected. These data, together with other mechanical and thermal property data, are given in Appendix B.

Resin batch 1039-23 was the first large batch from the last resin scale-up and gave $\sim$ 5-1/2#. Three samples were run with the now normal molding conditions of 60 minutes at 750°F under 5000 psi, modified to be sure that previous effects were real i.e, not just and artifact of the changing batches. Moldings 1028-109 and -110 were run at the 800°F temperature for 60 minutes and both cracked through the plate thickness. A modified molding cycle was used next (1028-111) in which 200 psi pressure was applied at the start of the cycle and kept throughout the cycle to finish at 800°F. The resin color remained orange-brown and, together with the low specific gravity of 0.948 and powdery texture, indicated insufficient cure. The standard cycle was repeated again (1028-112A) and apparently the resin was not smoothed adequately because both ends were thin, light in color and powdery. However, seven large moldings were made in succession without gross flaws according to NDT ultrasonic inspection. Six of these were sent to NASA Langely as part of the deliverable items.

The molding portion of this investigation required nearly 20 lb. of pyrrone resin molding powder to demonstrate that unfilled moldings of good to excellent mechanical and physical properties can be made. The scale up to large moldings (8-1/2 in. x 3-1/4 in. x 1/4 in.) from 5 in. x 1 in. x 1/4 in. moldings gave significant problems. Moldings with good physical properties and good very high temperature mechanical properties (900 and 1000°F) were made although the R.T., 500 and 700°F properties are only fair.

VI. FILLED PYRRONE MOLDINGS

The filled molding study consisted mainly of the addition of molybdenum disulfide and graphite to the moldings. Other fillers which were tried included carbon, alumina, cured pyrrone powder, silica, and industrial diamonds. The molding characteristics of the 5 x 1 x 1/4-in. bars are listed in Table XXIX.

Molybdenum disulfide (MoS_2) was introduced as a filler at the level of 20 percent by weight by adding it to the BSA solutions of both monomers during the molecular mixing step. MoS_2 was also introduced by two other methods both of which also gave a nice homogeneous mixture without apparent segregation. The second method of introduction was by addition of the MoS_2 to a 10 percent solution of the resin in formic acid. The solvent was removed by gentle heating at 125°F followed by $\sim$ 16 hours in a vacuum oven held at 150°F. The third method was to make a paste of oligomer route resin powder in a conventional route resin varnish (obtained from NASA Langley) with equal quantities of resin from each source. The MoS_2 was then mixed into this paste by hand and the resultant homogeneous mixture dried under vacuum. All MoS_2 mixtures were at 20 percent by weight of the total solids which is about the level of filler in commercial polyimide moldings claimed to have superior lubricity. The latter mixture dried to a dark brown-black glassy solid which was substantially more difficult to grind into powder. The good film forming properties of the high molecular weight conventional route resin is the most likely cause of this. However, except for slight differences in color, all three of the MoS_2 mixtures appeared visually identical. The molding behavior was substantially different among the three as shown by Table XXIX. All moldings were dark, well compacted disks but the varnish based molding powders gave much greater flash and much lower density moldings.

Graphite powder was used as a filler at the 20 to 25 percent weight level (Table XXIX). The first molding (1028-96) appeared visually well cured and without powdery spots but very low in specific gravity. The graphite did not appear exceptionally well dispersed with small silvery speckles showing on a sanded surface. This powder, coded BB-1, had only a moderatly small particle size with 50 percent between 200 and 300 mesh, and was mixed with the resin in a mortar and pestle to a uniform gray-black color. In an attempt to get better mixing a fugitive carrier was used while mixing the graphite powder with the resin for the next moldings. With acetone as the fugitive carrier the specific gravity rose to 1.40 and 1.44 for moldings 1028-107A and B. The 1.44 specific gravity corresponds to about 95 percent theoretical density. A third repeat of this condition (1028-117A) gave a specific gravity of 1.42 which indicates moderately good reproducibility. The latter three moldings were delivered to NASA Langley Research Center.

TABLE XXIX
MOLDING QUALITIES OF RESIN-FILLER MIXTURES

Molding Number	Resin Number	Type of Filler	Wt. of Filler %	Type of Filler-Resin Mixing	Wt. Loss in Molding %	Specific Gravity of Molding	Remarks
1028-77	478-138	MoS_2	20	BSA	13.1	1.44	Good; moderate flash
1028-74	478-147	MoS_2	20	Formic Acid	26.4	1.48	Good; moderate flash
1028-65	478-147	MoS_2	20	NASA Varnish	44.0	1.32	Good flow; greasy surface
1028-68	478-147	MoS_2	20	NASA Varnish	44.5	1.31	Fair; lots of flash
1028-72	478-147	MoS_2	20	NASA Varnish	40.5	1.33	Good; lots of flash
1028-96	1039-5	Graphite BB-1	25		7.5	1.22	
1028-107A	1039-23	"	20		19.4	1.40	Used acetone as carrier
1028-107B	1039-28	"	20		15.5	1.44	
1028-117A	1039-23	"	20		14.7	1.42	
1028-120A	1039-32	Graphite	20	water	18.8	1.36	Colloidal dispersion
1028-120B	1039-34	Graphite (fine)	15		15.2	1.45	
1028-120C	1039-34	"	15	Formic Acid	15.5	1.43	
1028-121A	1039-37	"	15		15.0	1.41	Mixed with mortar and pestle
1028-121C	1039-37	"	15		15.7	1.40	Mixed with mortar and pestle
1028-81	478-147	Carbon	50	Formic Acid	33.4	1.01	Good; little flash
1028-83	478-147	Alumina	50	Formic Acid	28.4	1.19	Fair; powdery and dry
1028-98	1039-4	Pyrrone Powder	20		14.0	1.30	$\frac{1}{2}$" diameter disk
1028-105	1039-12	Pyrrone Powder	50		10.0	1.22	$1\frac{1}{2}$ inch diameter disk
1028-61	478-138	Silica	50	BSA	10.2	1.09	Poor; dry and light colored
1028-106	1039-15 1039-20	Diamond	28.5		10.0	1.54	Good; well consolidated

Molding conditions: 775°F at 5,000 psi for 60 minutes

73

The relatively large size of the BB-1 graphite gave an aggregate type of appearance to the sanded surfaces of the molding. Another graphite, a 22 percent solids colloidal graphite in water, was mixed with sufficient resin to get a 20 percent graphite-80 percent resin mixture in water. Some water was added to decrease the thickness of the resulting dispersion for easier mixing. The wet mixture was dried under vacuum overnight and then ground in a mortar and pestle to a fine powder before molding under the same conditions as for the BB-1 filled moldings. The molding (1028-120A) had a lower specific gravity and greater evidence of graphite agglomeration than was seen in the previous BB-1 graphite filled molding (1028-117A). Perhaps the residual acid of the resin powder (either BSA or hydrolyzed anhydride groups) destroyed the dispersion. Previous attempts to dilute the pure graphite suspension in formic acid or BSA resulted in immediate agglomeration and precipitation. This molding was also delivered as part of the contract.

A third and much finer dry graphite powder was used as a filler. This graphite passed better than 90 percent through a 325 mesh screen compared with less than 30 percent through for the BB-1. Six 5 x 1 x 1/4-in. moldings were made with this graphite at the 15 percent level (Table XXIX). The first molding (1028-120B) was made in as nearly identical fashion as possible to the best of the BB-1 filled moldings. The 1.45 specific gravity corresponds to less than 2.5 percent void volume with the theoretical density at the 1.48 level for 15 percent loading. Even though the specific gravity was excellent, the graphite was not dispersed as well as desired. A sanded surface showed relatively large areas of silvery color indicating significant agglomeration of the graphite. Coating of the individual graphite particles was tried as a means of overcoming this problem of agglomeration. About one third of the resin required to make a molding was dissolved in formic acid and the solution mixed with the graphite powde. The formic acid was then evaporated off under vacuum, the pyrrone "coated" graphite broken up and then mixed with the rest of the resin in a mortar and pestle. The molding (1028-120C) had a slightly lower specific and no indication of better graphite dispersion. The last two moldings (1029-121A and 1018-121C) were made by dry mixing the graphite with a mortar and pestle as before. The moldings were as visually homogeneous as the earlier moldings made with this finer graphite, but the specific gravity was lower. The four moldings discussed above were delivered to NASA Langley Research Center.

Colloidal carbon at the 50 percent loading level gave a visually good looking molding (1028-81), dark with good flow and no powdering evident, although the specific gravity was low (Table XXIX). Alumina powder gave a molding (1028-83) of intermediate appearance, dark in color with higher density than the carbon but lower than the MoS_2 and also intermediate in the extent of powdery appearance. Colloidal silica was added to the BSA solutions as was done for the MoS_2. No segregation was evident during the precipitation and washing steps but the molding (1028-61) which was made with the silica was very poor. It had a dry, light colored appearance which suggested that the resin had not wet the silica surface.

74

Cured pyrrone resin in the form of dust from grinding test specimens was tried as a filler in moldings 1028-98 and 1029-105 at the 20 percent and 50 percent levels by weight respectively. The 20 percent level resulted in a moderately good density molding 1/2 in. in diameter with good color and integrity. The higher 50 percent loading gave a light colored, much lower specific gravity, and fragile molding. The second molding was 1-1/2 in. in diameter which could influence the molding properties but the higher level of filler is more likely to be the cause of the poorer properties.

Type RVG man-made industrial diamonds of 150 mesh were mixed dry with resin powder at 28.5 percent by weight and molded at 775°F for 60 min. under 5000 psi. The resulting specific gravity was 1.54 as shown for molding 1028-106 in Table XXIX. The sample had very good integrity and color but was not perfect visually as some porosity was visible. The high specific gravity of the filler gives a theoretical specific gravity of 1.69 so that the measured value of 1.54 corresponds to $\sim$ 9 percent void volume. Considerable difficulty was encountered machining flexural test strips from this molding. The diamonds in the molding wore off the smaller diamonds on the slitting saw causing it to heat and crack but no damage was done to the molding. After trying some carbide tipped slitting saws with negative results, ultra sonic machining succeeded though somewhat more frequent reshaping of the cutting tool was required.

Nine of the early filled moldings were tested for flexural properties at elevated temperatures and the data are shown in Table XXX. Along with the mechanical properties are listed the molding specific gravity and the theoretical specific gravity based on the listed filler content and 1.40 for pure resin. The theoretical specific gravity indicates how well densified the molding is and how the filler affects the molding process. None of the fillers appear to act as mechanical reinforcing fillers in these early moldings since the flexural strengths at 500°F are only 10 to 50 percent of the high average values shown in Appendix B while the resin content varied from 50 to 80 percent. The 700°F strengths values are better relative to these average values except for the carbon black fillers. The other 700°F strengths vary from 25 to 70 percent with the top end corresponding to full resin strength for the industrial diamonds where resin is also $\sim$70 percent by weight. A comparison of the 500°F modulus values with the high average values given in Appendix B shows all the filled modulus values at or below the unfilled values. The MoS_2 mixed in the BSA solution and precipitated and washed with the resin gave the greatest improvement in modulus with the three lower density MoS_2 NASA varnish samples about normal in modulus.

Graphite filled moldings made from resin ball milled for several days with the finer graphite powder though otherwise the same as the $5 \times 1 \times \frac{1}{4}$" moldings delivered to NASA appeared much more homogeneous in appearance of cross section with individual graphite particles much finer in size and evenly dispersed though specific gravity was not significantly higher. One of these, 1028-122B, was tested in flexure and gave the much higher strength and extreme modulus values shown in Table XXXI. In spite of the dramatic improvement in strength and modulus

TABLE XXX

Flexural Properties of Filled Pyrrone Molding

Sample No.	Filler	Filler Level %	500°F Strength psi	500°F Modulus psix10⁻⁶	700°F Strength psi	700°F Modulus psix10⁻⁶	900°F Strength psi	900°F Modulus psix10⁻⁶	Measured Specific Gravity	Theoretical Specific Gravity
1028-65	MoS$_2$ & NASA varnish	20	5,200	0.56					1.32	1.63
1028-68	MoS$_2$ & NASA varnish	20	7,420	0.68					1.31	1.63
1028-72	MoS$_2$ & NASA varnish	20	6,540	0.54					1.33	1.63
1028-77	MoS$_2$ im BSA	20	6,450	0.712	4,160	0.34			1.44	1.63
1028-81	Carbon black	50	1,880	0.377	66	0.003			1.01	1.63
1028-106	Industrial diamonds	28.5	8,170	0.54	8,730	0.38	2,790	0.137	1.54	1,69

TABLE XXXI

FLEXURAL PROPERTIES OF GRAPHITE FILLED PYRRONE MOLDING TYPICAL OF DELIVERABLE RODS

Sample No.	Filler	Filler Level %	500°F Strength psi	500°F Modulus psi x 10^{-6}	900°F Strength psi	900°F Modulus psi x 10^{-6}	Measured Specific Gravity	Theoretical Specific Gravity
1028-122B	Graphite Powder 90% 32 mesh	15%	8,350	1.51	2160	0.325	1.38	1.53
			11,100	1.81	2570	0.410		
			13,100	1.74				
	Average		10,800	1.67	2370	0.27		

77

the filler dispersion was not truly homogeneous so that further improvements should be possible.

Thirteen filled plates, 8½" x 3¼" x ¼", were molded from a ball milled mixture of fine graphite powder and pyrrone resin per the schedule for the delivered bars. The physical data on these moldings is shown in Table XXXII. The specific gravities though somewhat low show a consistency that indicates a reproducible process.

Since many of the use areas for commercially available polyimide moldings are in bearing uses, the wear characteristics of the graphite powder filled molding were looked at. Wear tests were started with paired samples of pyrrone-20 percent BB-1 graphite and 15 percent graphite loaded polyimide moldings. Pieces 0.400 in. wide and one inch long were machined with a one curved face which had a 3.25 in. diameter cylindrical surface to wear against a 3.25 in. diameter steel disk. The two test pieces had thermocouples embeded 0.104 in. and 0.164 in. from the wear surface for the pyrrone and the polyimide respectively. Both pieces were run at $\sim$ 100,000 PV for about two days. The equilibrium temperatures recorded by the thermocouples (after 8 hr. of running) were 200°F and 260°F for the pyrrone and the polyimide respectively. Since the thermocouple was closer to the wear edge for the pyrrone an even greater temperature differential is indicated.

TABLE XXXII

PHYSICAL DATA ON FILLED BARS

Molding #	Resin #	% Graphite	Wt. Gms.	Volume cc	Specific Gravity
1028-135A	1039-27	15	141.6260	103.0	1.375
1028-135B	1039-27	15	140.5	101.3	1.38
1028-136A	1039-27	15	138.8	100.8	1.38
1028-136B	1039-27	15	140.5	100.8	1.39
1028-137A	1039-27	15	140.0	103.1	1.36
1028-137B	1039-27	15	139.7	101.2	1.38
1028-138A	1039-27	15	142.4	102.6	1.39
1028-138B	1039-27	15	150.5	108.1	1.39
1028-138C	1039-27 1039-27+	15	145.3	104.0	1.40
1028-140A	1039-35-60	15	147.3	101.7	1.38
1028-140B	1039-35-60	15	154.0	110.3	1.40
1028-140C	1039-35-60	15	154.8	110.8	1.40
1028-141A	1039-35-110	15	153.8	109.9	1.40

VIII. CONCLUSIONS

Pyrrone polymers have been synthesized by means of novel oligomer route, and both filled and unfilled moldings have been made and subjected to mechanical and thermal tests.

The pyrrone molding powder was synthesized as short chain, low degree of polymerization (DP) oligomers of benzophenone tetracarboxylic acid dianhydride (BTDA) and tetraaminobiphenyl (DAB). One oligomer had a DAB molecule capped on either end by a BTDA molecule; the other oligomer was just the reverse. Each oligomer was synthesized separately in benzene sulfonic acid (BSA) at $170^\circ C$ $(443^\circ K)$, then mixed togehter in BSA, and the powder was precipitated from the resulting solution. Initially the powder was made in 100 gram batches but scale-up to five pound (2268 grams) batches was successful.

The low DP pyrrone powders were compression molded at temperatures of 700°-$800^\circ F$ $(644^\circ$-$700^\circ K)$, at pressures of 5,000-13,000 psi (34-90 MN/m^2), for one hour. The partially cyclized short chains cyclized more completely and combined to form longer chains. Although these oligomers generated only a third as much volatile material as the previous pyrrone molding powders, it was necessary to use glass fiber cloth as an escape path for the volatiles during molding. The flow and weight loss which were obtained during molding were proportional to the acidity of the powder. Moldings which were 5 x 1 x 1/4 inch (127 x 25 x 64 mm) were readily made. Large moldings (8-1/2 x 3-1/4 x 1/4 inch, 216 x 83 x 64 mm) often cracked in the press. Although several variations of the molding cycle were tried, the precise reason for the cracking was not determined. Particulate fillers, especially molbdenum disulfide and graphite, were added to the powder and both small and large moldings were made of the filled powder.

Flexural and thermal tests of pyrrone moldings were made to examine the effect of synthesis and molding process parameters, and to establish a body of reference data for future tests. The flexural strength and modulus of the best moldings were 17,500 and 920,000 psi (121 and 6,342 MN/m^2) at room temperature, and 3,000 and 250,000 psi (21 and 1,723 MN/m^2) at $1,000^\circ F$ $(811^\circ K)$. The test moldings had a weight loss of 26 percent after 1,000 hours of ageing in air at $600^\circ F$ $(589^\circ K)$, the flexural properties after ageing were scarcely affected.

The addition of fillers generally caused a reduction in both flexural strength and modulus with the exception being very fine graphite powder. The fine graphite when ball milled as a filler at 15% loading showed only a modest decrease in flexural strength but a large (2X) increase in modulus at $500^\circ F$. The apparent compatibility of the Pyrrones with lubricating type fillers indicate that the Pyrrone moldings may be useful as high temperature bearing materials.

Appendix A - Machinability of Pyrrone Moldings

Machining operations were attempted with a fly cutter single point tool, a two flute milling cutter, a four flute milling cutter, and alumina wheel and diamond wheels and slitting saws. The fly cutter always left a fractured edge when the cutter left the piece. The two flute cutter and the four flute cutter were much better with edge chipping much reduced at equivalent cutting edge speeds and surface removal rates. For example a 1 in. four flute cutter running at 600 rpm and taking a 0.015 in. cut per pass at a 1 in./min. feed rate showed edge chipping along 30 percent of the exit edge. The most efficient tools were the alumina wheels and diamond wheels for surface grinding, and the diamond slitting saws for rough sizing of samples. Typical conditions for using diamond grinding wheels to shape 1/4 in. diameter rods from 5 x 1 x 1/4 in. bars are given in Table A-I.

<center>TABLE A-I</center>

<center>MACHINING CONDITIONS FOR 1/4" DIAMETER RODS</center>

3" Diameter diamond grinding wheel
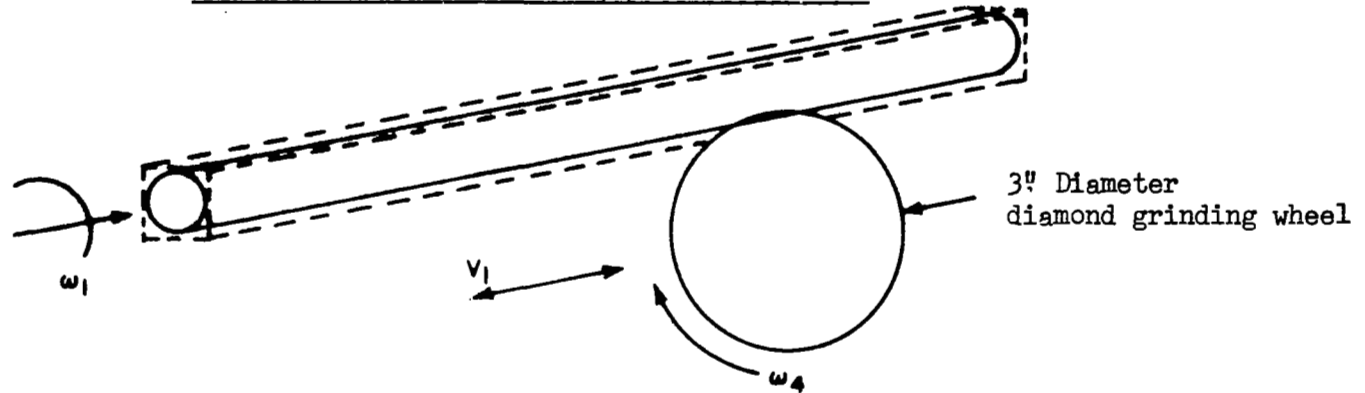
For roughing cut

Lathe spindle speed, W_1	= 1400 RPM
Dumore Grinder wheel speed, W_2	= 8300 RPM
Grinder wheel feed velocity, V_1	= 0.0185 inches/sec.
Depth of Grinder cut/pass, $\dfrac{\text{dia. initial-dia. final}}{2}$	= 0.030 inches

For Final Cut

Lathe spindle speed, W_1	= 1400 RPM
Dumore Grinder wheel speed, W_2	= 8300 RPM
Grinder wheel feed velocity, V_1	= $\sim$ 0.012 inches/sec.
Depth of Grinder cut/pass $\dfrac{\text{dia. initial-dia. final}}{2}$	= 0.005 inches

For final polish

Use 600 A wet or dry emery   cloth by hand

Appendix B - Pyrrone Molding Properties

Property determinations were made on pyrrone moldings in addition to those used for directing the contract research. In particular data on tensile and compressive properties as a function of temperature and thermal expansion to 600°F were obtained. Figures B-1 and B-2 show the average of the best seven values of flexural strength and flexural modulus, respectively, as a function of temperature. Table B-1 lists the tensile properties and Table B-II lists the compressive properties of the same molding as a function of temperature.

The tensile tests were made on a rectangular cross-section dog bone shape with both width and thickness reduced at the test section. The grip section was also reinforced with a thin phenolic laminate or aluminum bonded on with epoxy adhesive for the 500°F and room temperature test pieces respectively. In spite of this both the room temperature and 500°F samples failed at the shoulder. The transition area from the grip section to the test section was not finished as smoothly as the test section and thus failure may be an indication of notch sensitivity. The data are shown in Table B-I.

Compressive data were obtained at room temperature, 500°, 700°, 900°, and 1000°F and are shown in Table B-II. The failure mode appears to be the same at all temperatures; a brittle type shear failure as shown in Figure B-3. This type of failure without any flow at 900 and 1000°F is in sharp contrast to the many samples that have shown quite ductile behavior in flexure tests at these temperatures.

The thermal expansion of pyrrone molding 1028-61-A (ρ = 1.35) was measured from -200 to 600°F. The resulting curve is shown in Figure B-4. The data show that the pyrrones have about one half the expansion quoted for polyimide resin moldings of 25-35 micro inches per inch per degree Fahrenheit. The breaks in the curves are real in terms of the instrument sensitivity and repeatability but insufficient tests have been done on the pyrrones to say whether the position is a function of molecular structure or vagaries in the molding history. The fact that two samples from different resin batches have shown a break at about 240°F and 450-500°F indicate the breaks may be fundamental in nature and tied in with structure.

The static coefficient of friction between a ground pyrrone surface and smooth steel (Johansson gage block) was found to be 0.211 by the inclined plane method.

25,000

20,000

FLEXURAL STRENGTH, psi

15,000

OLIGOMER PROCESS PYRRONES (av. best 7)

10,000

1028-90

POLYIMIDE MOLDING

5,000

0

0   100   200   300   400   500   600   700   800   900   1000

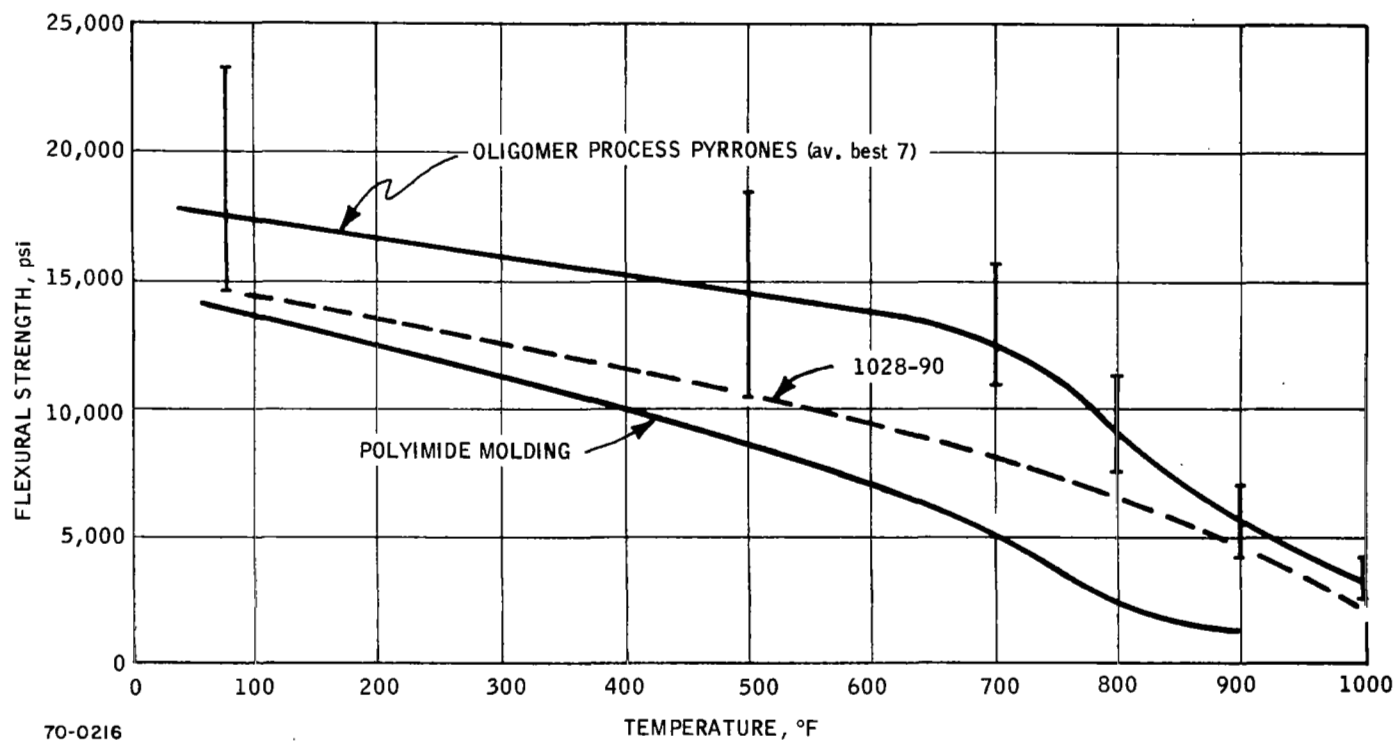70-0216

TEMPERATURE, °F
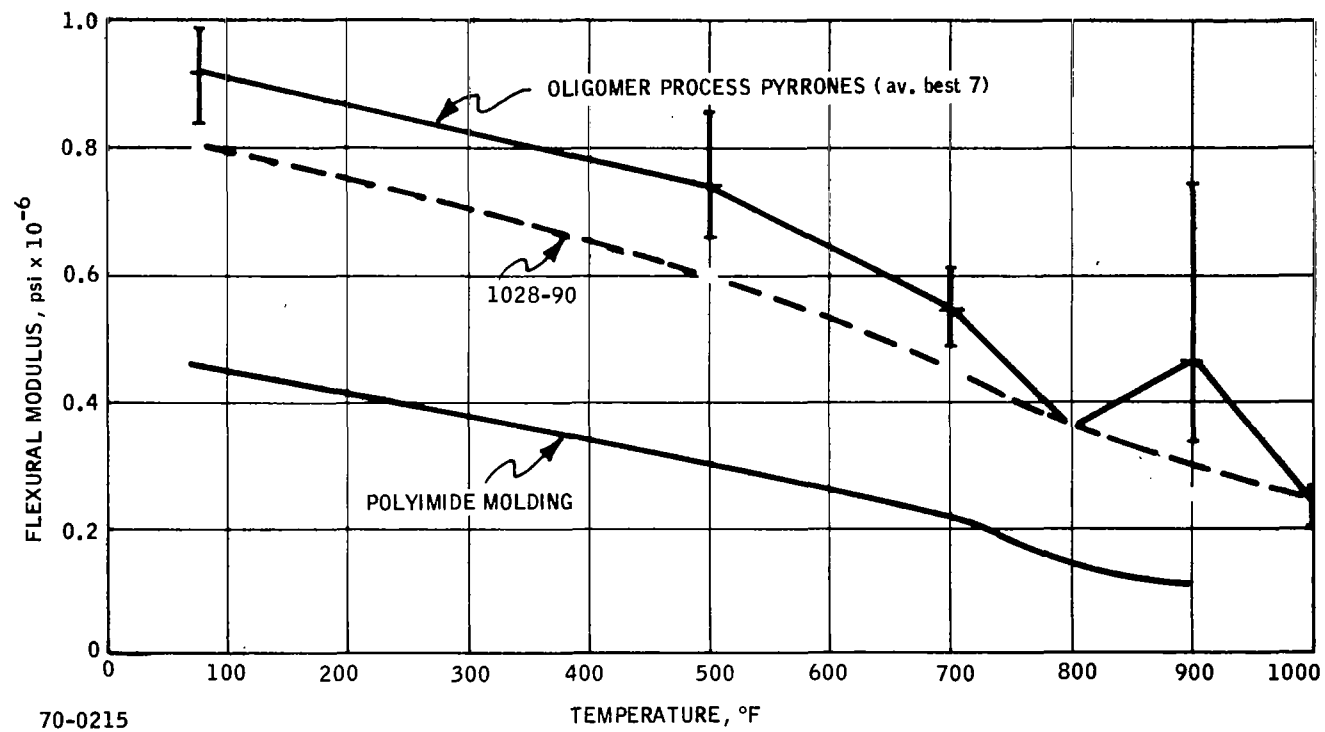
Figure B-1 FLEXURAL STRENGTH AS A FUNCTION OF TEST TEMPERATURE

Figure B-2 FLEXURAL MODULUS AS A FUNCTION OF TEST TEMPERATURE

TABLE B-I

TENSILE PROPERTIES OF PYRRONE MOLDINGS

Test Temperature $^\circ F$	Ultimate Strength Psi	Modulus psi x 10^{-6}	Strain to Failure %
75	8850*	0.783	1.19
500	6100*	0.727	1.13
700	2540	0.188	1.23
900	1420	0.139	1.12

*Indicates failure at shoulder

TABLE B-II

COMPRESSIVE PROPERTIES OF PYRRONE MOLDINGS

Test Temperature °F	Ultimate Strength psi	Modulus Psi x 10^{-6}	Strain to Failure %
75	23,500	0.760	3.56
500	14,600	0.410	3.90
700	5,280	0.304	1.53
900	3,750	0.340	2.67
1000	3,070	0.300	0.92

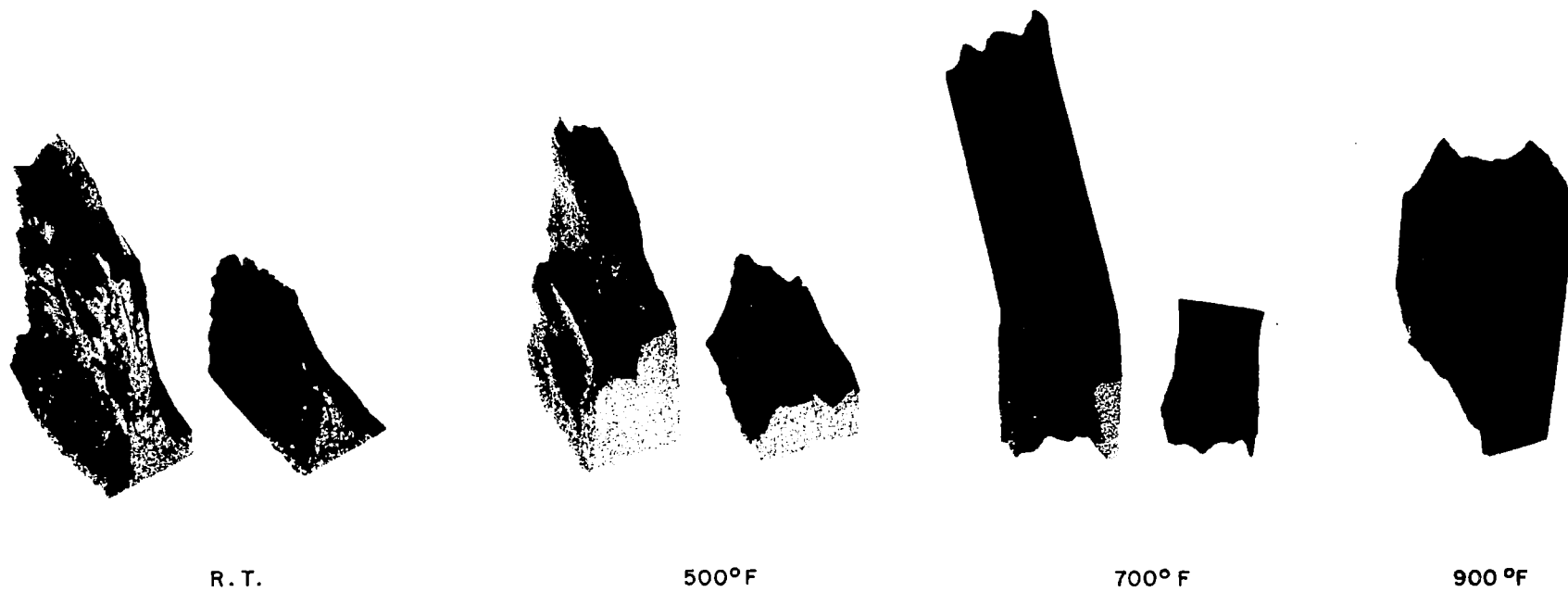R.T.   500°F   700° F   900 °F

Figure B-3 FAILURE MODE FOR COMPRESSION SAMPLES OF MOLDED PYRRONE
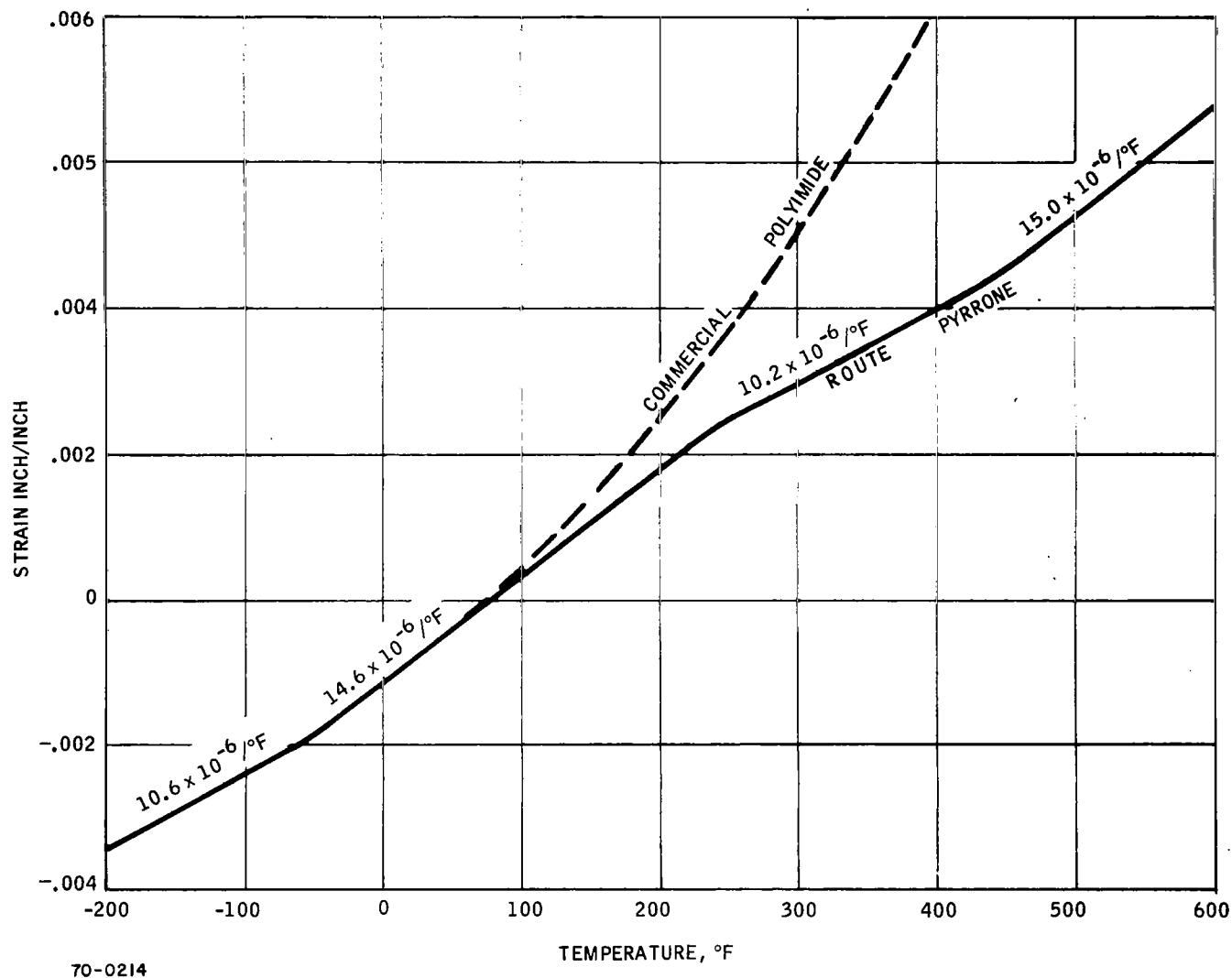AS A FUNCTION OF TEMPERATURE

70-0214

Figure B-4 THERMAL STRAIN AS A FUNCTION OF TEMPERATURE FOR AN OLIGOMER ROUTE
PYRRONE MOLDING AND A COMMERCIAL POLYIMIDE

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